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Belgium

Working Fluid Safety

Working Fluid Safety

Annex 20

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The Implementing Agreement for a Programme of Research, Development, Demonstration and Promotion of Heat Pumping Technologies (IA) forms the legal basis for the IEA Heat Pump Programme. Signatories of the IA are either governments or organizations designated by their respective governments to conduct programmes in the field of energy conservation.

Under the IA collaborative tasks or 'Annexes' in the field of heat pumps are undertaken. These tasks are conducted on a cost-sharing and/or task-sharing basis by the participating countries. An Annex is in general coordinated by one country which acts as the Operating Agent (manager). Annexes have specific topics and workplans and operate for a specified period, usually several years. The objectives vary from information exchange to the development and implementation of technology. This report presents the results of one Annex. Coordination of activities and assistance to Operating Agents is provided by the Technical Support Services Unit, the administrative arm of the Programme. The Programme is governed by an Executive Committee, which monitors existing projects and identifies new areas where collaborative effort may be beneficial.

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For further information about the IEA Heat Pump Programme contact the Technical Support Services Unit (TSSU) and for inquiries on heat pump issues in general contact the IEA Heat Pump Centre at the following address:

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EXECUTIVE SUMMARY

1. Working Fluid Safety

There is, today, considerable interest in the safety of refrigerants, much of it generated by the current search for alternative, less environmentally damaging working fluids for use with refrigeration units and heat pumps.

Refrigeration accidents are, fortunately, rare events. A recent assessment based on literature from Japan, the Netherlands and Norway has suggested that the risk of death from a refrigeration accident involving ammonia is 1×10^{-4} per installation per year. This is greater than the domestic natural gas risk and equivalent to the personal risk incurred by a 12-16 year old child (the less vulnerable age). The risk of injury is higher - $10\text{-}30 \times 10^{-4}$ per installation per year.

The number of accidents involving non-ammonia refrigerants appears to be much smaller, probably reflecting the fact that most of these fluids are non-toxic as well as non-flammable.

Refrigerants vary considerably in terms of their physical and safety properties. The safety standards adopted by individual countries also vary widely in terms of both their severity and their comprehensiveness. Nevertheless, safety remains a significant issue.

2. The Hazards Associated with Working Fluids

Incidents involving working fluids fall into three categories: fire, explosion and release. The ignition of a flammable working fluid gives rise to a fire which poses a hazard to persons in its vicinity. The type of fire can vary, depending on the type of release and the nature of the working fluid. Typical examples include jet flames, pool fires, fire-balls, and flash fires.

Explosions may be either mechanical or chemical in nature. When the contents of a vessel are suddenly released, the associated mechanical explosion gives rise to damaging pressure waves. In addition, the fragments derived either from the vessel or from pressure-wave damage to other objects, function as missiles, inflicting considerable damage on both people and equipment in the vicinity. When the release is associated with the formation of a flammable cloud, a chemical explosion may result, the degree of damage varying with the concentration of the vapour and its degree of confinement.

Intoxication and asphyxiation are also important considerations in the wake of an accident. The main mode of intoxication is by inhalation, and a distinction can be made between long exposure to low concentrations and a brief exposure to high (lethal) concentrations. Apart from the toxicity of the working fluid itself, the occurrence of a fire may result in the formation of toxic combustion gases. Asphyxiation may occur when the concentration of working fluid vapour prevents the transport of oxygen to the lungs.

Very cold working fluids can have an impact on both people and materials. They cause freeze burns when in contact with the skin and can give rise to significant levels of metal embrittlement after contact with metal surfaces.

3. Hazard Evaluation Using Indices

Two important indices have been developed as a means of general hazard evaluation:

- the DOW Fire and Explosion Index;
- the Toxicity Index.

The DOW Fire and Explosion Index makes it possible to quantify the expected damage resulting from potential fires and explosions and to identify the equipment most likely to contribute to the escalation of such an incident. The Index takes into account and quantifies three parameters:

- the material factor - the fire and explosion hazards which are inherent in the working fluid itself;
- the general process hazards that play a primary role in determining the scale of a loss accident;
- the special process hazards that contribute to the probability of such an accident.

It uses the results to generate a general index based on materials and process conditions. This index can then be used to compare different process units.

The Toxicity Index, unlike the Fire and Explosion Index, gives no information about the area of exposure or the degree of hazard. It is, however, valid for comparing installations. It is derived by multiplying the toxicity factor by the sum of the general process hazards factor, the special process hazards factor and a value of 2.

The application of these Indices is relatively simple. Fire and Explosion Indices calculated for an ethylene process storage unit, an ethylene compressor and an ammonia process storage unit show that the calculation requires only basic information about the installation and the process involved. The Toxicity Index is also simple to calculate, and worked examples for the ethylene and ammonia equipment described above indicate that the Index has a narrower range than its fire and explosion counterpart. The same examples demonstrate that toxic working fluids that are also flammable will be much more heavily penalised than others.

4. Models for Evaluating Specific Effects

A number of models have been derived to permit the calculation of various parameters:

- the total working fluid emission and its distribution between the various phases;
- the concentration of gases in the vicinity of a working fluid emission;
- the effects of pressure waves, heat radiation and the concentration of toxic gases;
- the impact on people.

These take into account the varying conditions that may arise in an accident such as whether the release is instantaneous or continuous, whether the release takes the form of a gas, a liquid or a combination of the two, whether the gases involved can be classed as neutral or heavy, and whether they are confined or unconfined.

The models have been applied to four specific scenarios involving, respectively, a non-toxic, non-flammable working fluid (freon 22), a non-toxic, flammable working fluid (propane), a toxic, flammable working fluid (ammonia) and a toxic, non-flammable working fluid (sulphur dioxide). The results have shown that accidents with non-toxic, non-flammable working fluids generate the minimum range of possible effects. Fluids which are flammable and/or toxic are more dangerous. However, the fire and explosion hazards are less for typical toxic, flammable working fluids than for those which are flammable only. However, while toxic, flammable fluids may be preferable from a flammability point of view, toxic effects can be expected for a released mass that is one or two orders of magnitude smaller than the concentration of a flammable working fluid with possible fire and explosion effects.

PART ONE

REFRIGERANTS: AN OVERVIEW

1. INTRODUCTION

1.1 Background and Scope of the Report

The search for alternative refrigerant working fluids has generated renewed interest in the safety aspects of these substances. There is a tendency in some quarters, for instance, to promote existing environmentally acceptable 'natural' fluids such as ammonia and propane. Most of these, however, pose significant safety problems.

This report is designed to investigate in an objective, scientific way the risks involved in refrigerant use. It achieves this both by examining accident records to date (Part 1) and by using quantitative effects analyses to determine the likely results of specific accident scenarios (Part 2).

The work was undertaken as Annex 20 of the Implementing Agreement Advanced Heat Pump Systems of the IEA. Countries participating in the study were:

- Belgium (Operating Agent);
- Japan;
- The Netherlands;
- Norway;
- Switzerland.

During the course of the work calculation programmes were developed and made available to the participants. This has made it possible for those participants to carry out independent studies of the likely effect of accidents involving, for instance, working fluids not covered in the study.

1.2 Report Structure

Part One of the report focuses on the characteristics and safety of refrigerants currently in use.
Chapter 2 examines the accident records of four countries, Japan, the Netherlands, Germany and Norway, and assesses the risk in each case. The nature of the literature means that the work has focused mainly on accidents involving the use of ammonia, although other refrigerants are considered where the information is available.

Chapter 3 lists the safety standards in operation at the national and international level, and provides a summary assessment of their comprehensiveness and severity. A more detailed comparison of the various standards is the subject of Annex 1.

Chapter 4 outlines the properties of the main refrigerant series, while Chapter 5 considers the alternatives that are now becoming available. The physical and safety properties of both the commonly and the less commonly used refrigerants are tabulated in Annex 2.
Part Two of the report focuses on hazard evaluation and accident assessment.

Chapter 6 examines the main types of hazard that are likely to be associated with an accident involving refrigerant working fluids. Consideration is given to fire, explosion, intoxication, asphyxiation and freezing.

Chapter 7 outlines the use of indices as a means of general hazard evaluation. It includes a full description of the DOW Fire and Explosion Index and how this is derived. It also examines the importance and derivation of an equivalent Toxicity Index. The application of both indices to specific industrial situations is the subject of Chapter 8.

Chapter 9 examines techniques appropriate for evaluating the specific effects of accidents. It considers topics such as emission and evaporation, the dispersion of gases, effects such as pressure waves, heat radiation and the concentration of toxic gases, and the vulnerability of personnel when exposed to these effects. Chapters 10-13 then consider the effects associated with accidents involving specific types of working fluid:

• Chapter 10	A non-toxic, non-flammable working fluid	freon 22 (R22)
• Chapter 11	A non-toxic, flammable working fluid	propane (R290)
• Chapter 12	A toxic, flammable working fluid	ammonia (R717)
• Chapter 13	A toxic, non-flammable working fluid	sulphur dioxide (R764)

All the results are obtained using the models described in Annex 3, and the conclusions to Part Two are presented in Chapter 14.

2. REFRIGERANT SAFETY EXPERIENCE

Refrigeration accidents are rare events. For instance, the Dutch Institute for Applied Scientific Research (TNO)[1] registered only 17 ammonia refrigeration accidents in the Netherlands over a period of 14 years.This implies that statistical information about, for instance, the most common accident causes is difficult to generate. However, both Japan and Germany have been able to provide useful statistics allowing some estimation of risk to be made. Information from the Netherlands and Norway, although less detailed, made some comparison possible.

2.1 Accidents Involving Ammonia

2.1.1 Recorded incidents

Japan

The data provided by the High Pressure Gas Safety Institute of Japan[2] showed that, during the 40 years between 1951 and 1990, 178 ammonia refrigeration accidents occurred in Japan, causing 15 deaths and 179 injuries [1]. Table 2.1 summarises the possible causes of these accidents.

Table 2.1 Causes of ammonia refrigeration accidents in Japan (1951-1990)

Cause	**%***
Rupture (most frequently condenser rupture) due to corrosion, fatigue etc	30
Human failure (during maintenance etc)	25
Liquid level indicator glass fails	12
Valve failure	12
Defective welding	9
Compressor exhaust valve failure	7
Liquid refrigerant isolated in piping or pressure vessel	4
Other (condenser cooling failure, rupture during scraping off of ice from the evaporator, safety failure, sparks etc)	10

* Because an accident can have several causes, the sum of the individual values does not equal 100%.

Netherlands

Information for the Netherlands came from three sources.

- In May 1991, TNO published a report about ammonia refrigeration accidents in the Netherlands [2]. Data were provided by FACTS, a database for industrial safety which relies for its information on newspaper articles and scientific literature. Seventeen accidents involving ammonia refrigeration installations were noted during the 14-year period between August 1977 and January 1991, involving five injuries and one fatality. No guarantee is given that these data are complete.

---

[1] TNO Netherlands Organization for Applied Scientific Research, Laan van Westenenk 501, 7300 AHApeldoorn, The Netherlands

[2] High Pressure Gas Safety Institute of Japan, Toranomon 3-6-2, Minato-ku, Tokyo

- In May 1992, TNO produced a report entitled *The Nature and the Extent of the Use of Ammonia as a Refrigerant in Dutch Food and Allied Products Industry* [3]. Two hundred and fifty-seven Dutch firms in this industrial sector were questioned. Of the 218 which responded:
  - 12 had no refrigeration system at all;
  - 103 used ammonia as a refrigerant;
  - 103 used non-ammonia refrigerants.

  Ninety-eight of the firms using ammonia answered the questions about accidents.
  - Nineteen had had an accident with their current installation.
  - Four of the accidents had caused injuries.

  NB: Three of the firms that did not answer the inquiry had had accidents that did not involve injuries.

  The average age of the installations was found to be about 14 years.

- In 1989, Spekking and Loos made a study of the safety of ammonia refrigeration systems (the VROM[1] inventory [4]). Thirty-seven firms using 42 ammonia refrigeration installations were examined with respect to the most recent CPR-13 regulations on the safety of refrigeration systems (1988) [5].
  This study made a hazard evaluation possible. A risk analysis was performed for each installation, and the personal risk involved (i.e. the probability of a person being killed in the neighbourhood of the installation) is shown in Table 2.2. When compared with the personal risk run by a 12-16 year old child (10^{-4} per year), risks smaller than 10^{-8} can be ignored.

Table 2.2 Personal risk from ammonia refrigeration systems according to VROM

Personal risk from ammonia refrigeration installation	**No of installations**
$> 10^{-5}$ per year	5
$\leq 10^{-5}$ and $> 10^{-6}$ per year	11
$\leq 10^{-6}$ and $\geq 10^{-8}$ per year	15
$< 10^{-8}$ per year	11

The exact values of the calculated risk for each installation are not known. Assuming that every installation carries the minimum risk for its group, the mean risk for all 42 installations is found to be:

1.5×10^{-6} per installation per year.

The contribution of the five installations in the first group to this mean risk is:

1.2×10^{-6} per installation per year.

This means that only 12% of the machinery is responsible for 82% of the total risk.
If only one of the installations carried a risk of 10^{-4}, it would be responsible for 66% of the entire risk.

---

[1] Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer, The Netherlands

Germany

According to the German Berufsgenossenschaft Nahrungsmittel und Gaststatten[1], the use of ammonia in Germany during the 1988-90 period caused 55 injuries (Table 2.3).

Table 2.3 Ammonia accidents in Germany (1988-1990): causes of injury

Cause of injury	No of injuries
Injured by explosion	4
Other (asphyxiation, frost-bite, intoxication etc)	51

The activity during which injuries occurred is given in Table 2.4.

Table 2.4 Ammonia accidents in Germany (1988-1990): activity during which injury occurred

Activity	No of injuries
Normal operation	1
Manual handling	5
Handling with instruments	45
Climbing etc	3
Control, inspection, installation	1

Not all the ammonia used is used as a refrigerant. The number of ammonia refrigeration injuries is much smaller than 55.

Norway

A Refrigeration-Energy-Food (REF)[2] document, published in February 1993 [6] mentions 18 ammonia refrigeration accidents in Norway between 1970 and 1991, causing six injuries and two fatalities. There were no accidents at all in heat pump plants.

World

An examination of scientific literature from various countries [7-14] revealed a lack of articles about ammonia refrigeration accidents.

The FACTS database referred to above includes 18 ammonia refrigeration accidents that occurred in countries other than the Netherlands. A further three were identified in the REF report. Table 2.5 gives an overview. Only four of these accidents involved an ammonia explosion.

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[1] Berufsgenossenschaft Nahrungsmittel und Gaststatten, Dynamostraße 7-9 6800 Mannheim, Germany

[2] Refrigeration-Energy-Food Consult AS, Gml Kongev 48, N-3040 Drammen, Norway

Table 2.5 Ammonia refrigeration accidents in different countries (1960-1991)

Country	No	Country	No
Germany	5	Sweden	1
USA	4	Japan	1
United Kingdom	3	Austria	1
Canada	2	Denmark	1
Spain	2	Indonesia	1

Apart from those recorded in the FACTS database, only four large ammonia refrigeration accidents have been registered:

- London 1961 [15];
- Paris 196? [15];
- Shreveport, Louisiana 1984 [16];
- Madison, Wisconsin 1991 [17].

All of them caused fire. In the London, Paris and Shreveport accidents an ammonia explosion occurred.

2.1.2 Risk calculation

Japan

Because the Japanese data are by far the most detailed, the risk calculation based on the Japanese report will be the most accurate.

The number of Japanese ammonia refrigeration systems is unknown. However, Schatten Ltd and Grencobel Ltd, the largest distributors of ammonia refrigeration systems in Belgium, estimate the number of ammonia refrigeration installations in Belgium at 300. Because ammonia refrigerators are mainly used in the food industry and almost never in air-conditioning systems, countries with the same level of development can be assumed to have the same number of ammonia refrigeration systems per million inhabitants. Japan has 120 million inhabitants compared with Belgium's 10 million, so the number of ammonia refrigeration installations in Japan is estimated at 3600.

The 178 accidents, 179 injuries and 15 deaths recorded for ammonia refrigeration over a 40-year period are equivalent to:

10^{-4} ammonia refrigeration deaths per installation per year;
12×10^{-4} ammonia refrigeration injuries per installation per year;
12×10^{-4} ammonia refrigeration accidents per installation per year.

Netherlands

Risk calculations for the Netherlands vary with the information source.

- Assuming that the Dutch population is about 1.4 times that of Belgium, the number of ammonia refrigeration systems in the Netherlands is estimated at about 420. The one fatality and five injuries occurring during the 14-year period covered by the FACTS database are equivalent to:

  1.7×10^{-4} ammonia refrigeration deaths per installation per year;
  8.5×10^{-4} ammonia refrigeration injuries per installation per year.

- According to the TNO inquiry, four injuries occurred with 103 ammonia refrigeration installations. The average installation age was 14 years. The risks identified were as follows:

  28 x 10^{-4} ammonia refrigeration injuries per installation per year;
  150 x 10^{-4} ammonia refrigeration accidents per installation per year.

  No-one was killed according to the TNO survey.

  In the VROM inventory the risk calculation was made not on the basis of statistical data but with the aid of a mathematical program (NH3). The calculations showed:

  0.015-0.15 x 10^{-4} ammonia refrigeration deaths per installation per year.

  This value is 10-100 times smaller than those observed in the other two investigations.

Germany

Because German statistical information deals with all ammonia accidents it is impossible to calculate the ammonia refrigeration risk. However, using the assumptions made in other countries for the number of installations and multiplying the value obtained by the Japanese ammonia refrigeration risk, it is possible to calculate the expected number of ammonia refrigeration injuries.

The German population of about 78 million is 7.8 times that for Belgium. The number of ammonia refrigeration installations is therefore assessed at about 2340. Assuming 12 x 10^{-4} injuries per installation per year, the risks can be calculated as:

2.8 ammonia refrigeration injuries per year (nine injuries over three years).

This is a much smaller figure than the 55 ammonia injuries recorded (Section 2.1.1).

Norway

It is estimated that there are about 1200 refrigeration installations in Norway. This large number is mainly due to the Norwegian fish industry. The 18 recorded ammonia refrigeration accidents, which caused six injuries and two fatalities, are equivalent to:

0.8 x 10^{-4} ammonia refrigeration deaths per installation per year;
2.4 x 10^{-4} ammonia refrigeration injuries per installation per year;
7.2 x 10^{-4} ammonia refrigeration accidents per installation per year.

2.1.3 Conclusion

Table 2.6 gives an overview of the ammonia refrigeration risk. The Japanese, FACTS and TNO results were obtained using the assumption that the number of ammonia refrigeration installations per million inhabitants is the same as the estimate for Belgium. The latter, at 300, is, of course, a rough estimate.

Table 2.6 Overview of calculated risk for ammonia refrigeration installations

Country		Deaths per installation per year (10^{-4})	Injuries per installation per year (10^{-4})	Accidents per installation per year (10^{-4})
Japan		1	12	12
Netherlands	FACTS	1.7	8.5	–
	TNO	–	28	150
	VROM	0.015-0.15	–	–
Norway		0.8	2.4	7.2

The results (excluding the VROM results) can be further summarised as follows:

The ammonia refrigeration risk is:
1 x 10^{-4} deaths per installation per year
10-30 x 10^{-4} injuries per installation per year
10-150 x 10^{-4} accidents per installation per year

The VROM results did not make use of statistical information and represent an underestimation of the risk.

The risk of death is equivalent to the personal risk incurred by a 12-16 year old child (the less vulnerable age). The risk of injury is fairly high.

2.2 Accidents Involving Other Refrigerants

Germany

According to the German Berufsgenossenschaft Nahrungsmittel und Gaststatten, the use of non-ammonia refrigerants in Germany during the three-year period 1988-1990 caused four injuries. Table 2.7 gives the causes of injury The injuries occurred only during handling with instruments.

Table 2.7 Non-ammonia refrigeration accidents in Germany (1988-1990): causes of injury

Cause of injury	No of injuries
Injured by explosion	1
Other (asphyxiation, frost-bite, intoxication etc)	3

Norway

In Norway, between 1970 and 1991, seven non-ammonia refrigeration accidents occurred [6]. Table 2.8 gives an overview of the accidents and their efects. One of the R22 accidents happened on board ship.

Table 2.8 Non-ammonia refrigeration accidents in Norway (1970-1991)

Refrigerant	No of accidents	No of unconscious people	No of injured people	No of fatalities
R22	7	4	1	3
R728 (N_2)	1	0	0	1

World

An examination of the literature [7-14) revealed no articles about non-ammonia refrigeration accidents. The Norwegian report [6] mentions two R22 accidents apart from the Norwegian accidents:

- Anchorage, USA 1990: one fatality;
- Hawaii 1991: two fatalities; on board ship.

Conclusion

The number of accidents with non-ammonia refrigerants is much smaller than the number of ammonia refrigeration accidents. This may be due to the fact that most of the former are non-toxic as well as non-flammable. They include the most commonly used refrigerants R11, R12, R22, R500 and R502.

2.3 Comparison with the Risk of Using Natural Gas

In October 1992, a safety report on the use of natural gas was published by the Dutch Centre of Gas Technology (GASTEC). This presented an overview of natural gas accidents in the Netherlands in the 1982-1991 period [18].

The report listed 778 accidents involving natural gas, of which 72 involved fatalities (Table 2.9). The total number of people killed was 101.

Table 2.9 Natural gas accidents in the Netherlands (1982-1991)

Type of accident	Total number of accidents	No of fatal accidents
Installation accidents	705	70
Distribution accidents	73	2
Total	778	72

For the average of around 5.4 million connections in existence during the 1982-1991 period these figures represent:

1.4×10^{-5} accidents per connection per year or one per year for every 70,000 connections;

1.3×10^{-6} fatal accidents per connection per year or one per year for every 750,000 connections;

1.9×10^{-6} fatalities per connection per year or one per year for every 530,000 connections.

Although these risks appear lower than those for ammonia refrigeration, it should be clear that the comparison being drawn is between domestic natural gas safety and industrial ammonia refrigeration safety.

2.4 Conclusion

The ammonia refrigeration risk must not be underestimated. It is much greater than the domestic natural gas risk and about the same as the personal risk of a 12-16 year old child.

The number of accidents involving non-ammonia refrigerants appears to be much smaller than the number of ammonia refrigeration accidents.

However, it is difficult to draw specific conclusions from the statistical information given. It is obvious that the accident data for ammonia installations relate to industrial systems. Equivalent data for non-ammonia industrial installations are almost non-existent, leading to the conclusion that the risks associated with non-ammonia industrial systems are several orders of magnitude lower than those for ammonia systems. In view of the fact that the number of non-ammonia systems is considerably larger than the number of ammonia systems, the risk of fatalities with the former is estimated to be less than 10^{-5} per installation per year. When considering the application of flammable refrigerants (propane etc) in the domestic sector, the fatal risk rates (10^{-7} to 10^{-8} per application per year) are considerably lower than those associated with the use of natural gas and those encountered during everyday life (10^{-4}).

3. REFRIGERATION STANDARDS

National and international standards on the safety requirements of mechanical refrigeration systems are already in force in many countries and have a significant role to play in the levels of safety achieved.

However, an examination of the standards applied in ten countries and internationally [19-32] showed not only that the concepts involved often differ from one country to another, but also that items extensively dealt with in one standard do not appear in another. Nevertheless, a comparison of standards has been attempted. The standards involved are listed in Table 3.1. Details of the comparison are presented in Annex 1 with a summary of the topics covered in Table 3.2.

Table 3.1 National and international standards examined

Country		Documentation
United Kingdom	BS 4434	British standard, British Standards Institution, UK (BSI)
Belgium	NBN E35-001	Belgian standard, Belgisch Instituut voor Normalisatie, Belgium (NBN)
Netherlands	NEN 3380	Dutch standard, Nederlands Normalisatie Instituut, The Netherlands (NEN) '*Eisen behorende bij het besluit ozon aantastende stoffen*', TNO, The Netherlands (TNO)
Switzerland	SN 25130	Swiss standard, Societe Suisse des Constructeurs de Machines, Switzerland (SN)
USA	ASHRAE 15-1989-R	American standard, American Society of Heating, Refrigeration and Air-Conditioning Engineers, US (ASHRAE)
Japan		'*Japanese Regulations on Refrigerants*', Japan (JR)
	KHKS 0402	Facility standard for Refrigeration Units, High Pressure Gas Safety Institute, Japan (KHK)
	MITI Ordonance	High Pressure Gas Control Law, Japan (MITI) '*Supplementary Standard for Refrigeration Safety Regulations*', Japan (SSRSR)
Germany	DIN 8975	German standard, Deutsches Institut fur Normung, Germany (DIN)
Sweden	Svesk Kylnorm	Swedish standard, Kylbranchens Samarbetsstifelse, Sweden (SK)
Norway	Norsk Kuldenorm	Norwegian standard, Samarbeidsutvalget for Kuldebransjen, Norway (NK)
France	NF E35-400	French standard, Association Francaise de Normalisation, France (NF)
International	ISO-DIS-5149	International standard, International Organisation for Standardisation (ISO)

Table 3.2 Topics examined by each standard

Topic	BSI	NBN	NEN	SN	ASHRAE	ISO	JN	DIN	SK	NK	NF
Specific dangers and scope	•	•	•	/	/	•	?	•	•	•	•
Refrigerant classification	•	•	•	•	•	•	•	•	•	•	•
System classification	•	•	•	•	•	•	•	/	•	•	•
Occupancy classification	•	•	•	•	•	•	•	/	•	•	•
Maximum charge of refrigerants	•	•	•	•	•	•	?	/	•	•	•
Pressure - design, protection, testing	•	•	•	/	•	•	•	•	•	•	•
Machinery room	•	•	•	•	•	•	•	/	•	•	•
Alarm and detection	•	•	•	•	•	•	•	/	•	•	•
Electrical installation	•	•	•	•	•	•	•	/	•	•	•
Instrumentation	•	•	•	/	/	•	?	•	•	•	•
Materials, piping, fittings	•	•	•	•	•	•	•	•	•	•	•
Marking, certification, instruction, maintenance	•	•	•	/	•	•	•	•	•	•	•
Miscellaneous special requirements	•	•	•	•	•	•	•	•	•	•	•

KEY
• Topic examined
? Insufficient information available
/ Topic not examined

The standards investigated have also been evaluated. A good safety standard has to be strict as well as complete, and Table 3.3 compares specific items in terms of their severity as well as their extensiveness. It should be clear, however, that this evaluation is based on only a limited number of regulations. It is also somewhat subjective in its approach.

Table 3.3 Evaluation of standards

Topic	BSI	NBN	NEN	SN	ASHRAE	ISO	JN	DIN	SK	NK	NF
Specific dangers	3	3	0	0	0	3	3	0	0	0	0
Scope	3	3	3	0	0	3	1	3	3	3	3
Small systems	3	3	3	0	0	3	3	0	3	3	2
HCFCs	0	3	0	0	3	0	0	3	3	3	0
Group 1	1	1	1	1	3	1	2	0	2	1	1
Group 2	3	3	3	3	3	3	3	0	3	3	3
Group 3	3	3	3	3	3	3	2	0	1	2	3
Standard pressure vessels	3	3	3	0	3	3	3	3	3	3	3
Strength repeat test	3	3	0	0	0	3	0	3	0	0	0
Pressure (general)	3	3	3	0	3	3	3	3	3	3	3
Machinery room	3	3	3	3	3	3	3	0	2	2	3
Alarm and detection	2	2	1	1	2	2	3	0	3	3	1
Electrical installation	2	3	2	2	3	2	3	0	2	2	2
Instrumentation	2	2	2	0	0	3	3	2	1	2	2
Materials and welding	3	3	3	0	3	3	3	3	3	3	1
Pipes and fittings	3	3	3	3	2	3	3	2	2	2	3
Marking, instruction and certification	2	3	3	0	1	3	2	3	3	3	3
Refrigerated spaces	3	3	3	0	0	3	3	0	3	3	3
Charging and discharging refrigerants	2	3	3	0	2	2	0	3	1	1	1
Safety provisions for personnel	3	3	3	0	1	3	2	1	3	3	1
Total	**50/60**	**56/60**	**45/60**	**16/60**	**35/60**	**52/60**	**45/60**	**29/60**	**44/60**	**45/60**	**38/60**

KEY

0	Item not treated in this standard
1	Less elaborate/less restrictive treatment of topic
2	Quite good treatment of topic
3	Best possible treatment of topic

4. THE PROPERTIES OF REFRIGERANTS

4.1 Introduction

The search for alternative refrigerants as initiated by the Montreal Protocol has given rise to a renewed discussion on the health and safety of refrigerants. Formerly only the safety and thermodynamic properties were important, but today's interests include the influence of the refrigerant upon the environment.

Important safety aspects to be considered include:
- atmospheric boiling point;
- toxicity and mutagenic properties;
- flammability and explosion properties.

The atmospheric boiling point is important as it determines the working pressure. High working pressures imply high emission rates in the case of system ruptures.

The influence of the refrigerant upon the environment is a function of:
- its influence on the ozone layer;
- its ozone depletion potential (ODP);
- its influence on the greenhouse effect;
- its greenhouse warming potential (HGWP).

An interesting approach in this respect is the one made by McLinden and Didion [33 to 34]. They represent refrigerants of the methane series (one carbon atom), the ethane series (two saturated carbon atoms), the ethylene series (two unsaturated carbon atoms) and the propane series (three saturated carbon atoms) in triangular form. Methane, ethane, ethylene and propane are placed at the top of their respective triangles. The number of chlorine (Cl) atoms increases along the right-hand side of the triangle - CCl_4, C_2CL_6, C_2Cl_4, C_3Cl_8 etc - while the number of fluorine (F) atoms increases along the left-hand side of the triangle - CF_4, C_2F_6, C_2F_4, C_3F_8 etc. The base of any triangle contains fully halogenated hydrocarbons, going from CCl_4 to CF_4, etc. At each step along the selected base a Cl atom is replaced by an F atom.

4.2 Properties of the Methane Series

Refrigerants of the methane series possess only one carbon atom. When represented in triangular format as described above (Figure 4.1), the following conclusions can be drawn:

- the boiling point increases to the right and downwards;
- toxicity increases to the right;
- the upper refrigerants (R50, R40, R41, R31 and R32) are explosive;
- only refrigerants in the two lowest rows have an ODP differing from zero.

Figure 4.1 The methane series

				R50 -162°C 4.9 - 15.9 % 16 g/mol 0 /				
			R40 -24°C 8 - 18 % 50 g/mol 0 50 ppm		**R41** -78°C ? - ? % 34 g/mol 0 ? ppm			
		R30 41°C / 85 g/mol 0 500 ppm		**R31** -9°C ? - ? % 69 g/mol 0 ? ppm		**R32** -52°C ? - ? % 52 g/mol 0 ? ppm		
	R20 61°C / 119 g/mol ? 50 ppm		**R21** 9°C / 103 g/mol 0.04 1000 ppm		**R22** -41°C / 86 g/mol 0.05 1000 ppm		**R23** -84°C / 70 g/mol 0 /	
R10 77°C / 171 g/mol ? 10 ppm		**R11** 24°C / 137 g/mol 1 1000 ppm		**R12** -30°C / 121 g/mol 1 1000 ppm		**R13** -81°C / 105 g/mol 0.45 /		**R14** -128°C / 88 g/mol ? /

refrigerant name
atmospheric boiling point (°C)
explosion limits (vol %)
molecular mass (g/mol)
ODP (-)
TLV-value (ppm)

LEGEND

? = insufficient information
/ = value does not exists (e.g. non-flammable or non-toxic)

4.3 Properties of the Ethane Series

Refrigerants of the ethane series possess two carbon atoms and six non-carbon atoms. The latter are either hydrogen (H), fluorine or chlorine. The position of these non-carbon atoms can determine the properties of the molecule (isomerism), and a distinction is often made between two, three or more isomer forms by appending the character a, b, c etc. Optical isomerism is not taken into account.

The ethane triangle is shown in Figure 4.2. The conclusions that can be drawn are similar to those for methane.

Figure 4.2 The ethane series

refrigerant name
atmospheric boiling point (°C)
explosion limits (vol %)
molecular mass (g/mol)
ODP (-)
TLV-value (ppm)

LEGEND

R170
-89°C
2.9 - 13 %
30 g/mol
0
/

R160	**R161**
12°C	-78°C
3.7 - 12 %	? - ? °C
66 g/mol	48 g/mol
0	0
1000 ppm	? ppm

R150,a	**R151,a**	**R152,a**
84°C 60°C	53°C 16°C	-31°C -25°C
6.2-16% 5.6-16%	?-?% ?-?%	?-?% ?-?%
99 g/mol	82 g/mol	66 g/mol
0	0	0
20 ppm 100 ppm	? ppm	? ppm

R140,a	**R141,a,b**	**R142,a,b**	**R143,a**
114°C 61°C	76°C ?°C 9°C	35°C ?°C -41°C	5°C -84°C
/ 8-15.5%	?-?% ?-?% ?-?%	?-?% ?-?% 4.4-18.5%	?-?% 9.2-18.4%
133 g/mol	116 g/mol	100 g/mol	84 g/mol
0	0	0	0
10 ppm 200 ppm	? ppm ? ppm 500 ppm	? ppm ? ppm /	/ /

R130,a	**R131,a,b**	**R132,a,b,c**	**R133,a,b**	**R134,a**
146°C 131°C	103°C ?°C 88°C	59°C ?°C 47°C	17°C ?°C 12°C	-19°C -26°C
/	/	/	/	/
169 g/mol	151 g/mol	135 g/mol	118 g/mol	102 g/mol
0	0	0	0	0
1 ppm ? ppm	? ppm	? ppm	? ppm	? ppm 1000 ppm

R120	**R121,a**	**R122,a,b**	**R123,a,b**	**R124,a**	**R125**
162 °C	117 °C 116°C	72°C 73°C ?°C	29°C ?°C ?°C	-12°C -10°C	-48°C
/	/	/	/	/	/
202 g/mol	186 g/mol	169 g/mol	153 g/mol	137 g/mol	120 g/mol
0?	0?	0?	0.016	0.02	0
5 ppm	? ppm	? ppm	100 ppm ? ppm ? ppm	500 ppm ? ppm	1000 ppm

R110	**R111**	**R112,a**	**R113,a**	**R114,a**	**R115**	**R116**
185°C	137°C	93°C 91°C	48°C 46°C	4°C 4°C	-39°C	-78°C
/	/	/	/	/	/	/
237 g/mol	220 g/mol	204 g/mol	187 g/mol	171 g/mol	155 g/mol	139 g/mol
?	?	?	0.8	1	0.6	?
? ppm	? ppm	? ppm	1000 ppm ? ppm	1000 ppm ? ppm	/	/

? = insufficient information
/ = value does not exists (e.g. non-flammable or non-toxic)

4.4 Properties of the Propane Series

The propane triangle is only partially known. Although it is almost impossible to list the properties of all the isomeric forms, their likely behaviour can be estimated on the basis of data from the methane and ethane triangles. Figure 4.3 illustrates the boiling point where known.

Figure 4.3 The propane series

refrigerant name
atmospheric boiling point (°C)

LEGEND

R290
-42°C

R280 **R281**
47°C -9 / -3°C

R270 **R271** **R273**
70 / 125°C ? 0 / 8°C

R260 **R261** **R262** **R263**
156°C 67°C 55 / 56°C -12°C

R250 **R251** **R252** **R253** **R254**
? ? 81 / 70°C 45°C ?

R240 **R241** **R242** **R243** **R244** **R245**
? ? ? 76 / 71 / 48°C ? -17 / 1°C

R230 **R231** **R232** **R233** **R234** **R235** **R236**
? ? ? ? ? ? 0 / 1 / 6 / 10°C

R220 **R221** **R222** **R223** **R224** **R225** **R226** **R227**
? ? ? 85°C ? 50°C ? -17 / -18°C

R210 **R211** **R212** **R213** **R214** **R215** **R216** **R217** **R218**
? ? ? ? 14°C ? 36°C -2 / -2°C -36°C

? = insufficient information

4.5 Properties of the Ethylene series

Unsaturated carbon combinations are much more reactive and toxic than saturated ones. For instance, a study of the ethylene triangle (Figure 4.4) shows that R1110 is probably the only refrigerant in the series which is non-explosive. This series also contains trans-cis isomeric forms. For instance, trans-1.2-dichloroethene or trans R1130 has an atmospheric boiling point equal to 48°C, whereas the cis-form boils at 60°C.

Figure 4.4 The ethylene series

R1150
-104°C
3 - 33%
28 g/mol
0
/

refrigerant name
atmospheric boiling point (°C)
explosion limits (vol %)
molecular mass (g/mol)
ODP (-)
TLV-value (ppm)

LEGEND

R1140
-14°C
3.8 - 31%
63 g/mol
0
? ppm

R1141
-51°C
2.9 - 29%
46 g/mol
0
/

R1130
48 / 60 / 37°C
5.6 - 11.4%
97 g/mol
0
200 ppm

R1131
?°C
? - ?%
81 g/mol
0
? ppm

R1132
-84°C
5.5 - 21%
64 g/mol
0
? ppm

R1120
86°C
7.6 - 90%
132 g/mol
?
50 ppm

R1121
?°C
? - ?%
115 g/mol
?
? ppm

R1122
-19°C
? - ?%
99 g/mol
?
? ppm

R1123
?°C
? - ?%
82 g/mol
?
? ppm

R1110
121°C
/
166 g/mol
?
50 ppm

R1111
?°C
?
150 g/mol
?
? ppm

R1112
19°C
?
133 g/mol
?
? ppm

R1113
-28°C
24 - 40%
117 g/mol
?
/

R1114
-76°C
?
100 g/mol
?
/

? = insufficient information
/ = value does not exists (e.g. non-flammable or non-toxic)

4.6 Properties of Other Refrigerants

Of the other refrigerants illustrated in Figure 4.5, ammonia is by far the most important.

Figure 4.5 Other important refrigerants

R600 (butane)
-0.5°C
1.8 - 8.4%
58 g/mol
0
? ppm

R1270 (propene)
-48°C
2 - 11%
42 g/mol
0
? ppm

R600a (isobutane)
-12°C
1.6 - 8.5%
58 g/mol
0
? ppm

R764 (SO_2)
-10°C
/
64 g/mol
0
? ppm

R611 (CH_3CO_2H)
31°C
4.5 - 20%
60 g/mol
0
? ppm

R717 (ammonia)
-33°C
15 - 27%
17 g/mol
0
? ppm

R12B1 ($CBrClF_2$)
?°C
/
164 g/mol
3
? ppm

R13B1 ($CBrF_3$)
-58°C
/
149 g/mol
10
? ppm

RC318 (octafluorocyclobutane)
-6°C
/
200 g/mol
0 ?
? ppm

R744 (CO_2)
-79°C
/
44 g/mol
0
? ppm

refrigerant name
atmospheric boiling point (°C)
explosion limits (vol %)
molecular mass (g/mol)
ODP (-)
TLV-value (ppm)
LEGEND

? = insufficient information
/ = value does not exists (e.g. non-flammable or non-toxic)

Further details of the properties of working fluids are given in Annex 2.

5. THE SEARCH FOR ALTERNATIVE REFRIGERANTS

By the year 2010, R11, R12 and R114 have to be replaced by less environmentally harmful HCFC and HFC refrigerants. Alternatives are required to have the same atmospheric boiling point as the original refrigerant in order to retain the same working pressures. Toxicity and flammability should be as low as possible, as should their harmful influence upon the environment.

5.1 Alternatives for R12

The refrigerant R12, which boils at -30°C at atmospheric pressure, is frequently used as a refrigerant at temperatures between +50°C and -30°C (the same temperature limits as ammonia). R12 has, however, a better compressibility than ammonia, making possible the use of centrifugal compressors. It is also non-flammable and almost non-toxic. Its effect on the environment, however, is significant. R12 has an ozone depletion potential of 1. This means that the accumulated damage caused during its atmospheric life is as great as that of the reference refrigerant R11.

5.1.1 Non-flammable alternatives

The most promising alternatives to R12 which are non-explosive, not very toxic and with a limited ODP are:
- R22;
- R134a;
- R125.

Certain refrigerant mixtures are also being considered.

R22 has a smaller ODP than R12, but is still ozone depleting. Although it does not offer a final solution to the CFC problem, it can be used as a transitional refrigerant.

R134a is universally regarded as the most promising successor to R12. It has an HGWP that is small compared with that for R11 and R12, but which is still large compared with the flammable R152a [37].Toxicological tests have not advanced as far as, for instance, with R123, but it does not have a high acute toxicity [38]. Problems with lubricants also seem to have been solved. Instead of polyalkylene glycol, which absorbs water and can be very corrosive, ester oil is recommended. The use of this refrigerant in small refrigerators is satisfactory [39, 40].

R125 has a large HGWP (approximately equivalent to that of R11) and a low boiling point. It is not regarded as an alternative to R12 except in mixtures.

Non-explosive mixtures of explosive and non-explosive refrigerants can also be made. A mixture of R134a and R152a remains non-flammable up to an 18% concentration of R152a. One advantage of this mixture is its low HGWP compared with pure R134a (R152a has an HGWP of 0.029). In 1993, Bauknecht were intending to market some refrigerators with this mixture as the working fluid [41, 42].

Mixtures of R23 and R152a can contain up to 33% R152a [43]. It should be noted, however, that this mixture is azeotropic: when a leak occurs, the composition of the mixture will change. During the maintenance of industrial systems, 30-50% of the entire refrigerant mass may have to be replaced. It is important to ensure that the changed composition of the mixture does not result in a capacity loss. However, there is no danger of the mixture inside the refrigerator becoming explosive.

The three-component mixture using R32, R125 and R134a is also promising. An excellent article on the optimal choice of the concentrations in a three-component mixture is one by Powell [37]. This contains a method for determining, given the desired boiling point of the refrigerant, the concentrations of the non-flammable mixture for which the HGWP is minimal.

Some other mixtures, for example those using R22, have an ODP differing from zero [41, 44-46]. Mixtures using R143a are not recommended because of their large HGWP.

5.1.2 Flammable alternatives

A recent investigation into the safety of flammable refrigerants in domestic refrigerators by James and Missenden involved replacing R12 with **R290 (propane)** in a domestic refrigerator [47, 48]. Apart from the astonishing result that the coefficient of performance (COP) of the installation did not decrease (better results were actually recorded), flammability and combustion tests highlighted the limited danger involved in the use of propane in refrigerators of this type. Only 40 g of propane were needed to replace 100 g of R12, and only 14 g could escape into the refrigerated enclosure when a hole was made in the evaporator. Flame duration was too short to cause surface pyrolysis.

Ammonia (R717) occupies a special place in the series of flammable refrigerants. There is long experience of its use, it is cheap and it is well known. In addition, leaks are easily detected by humans at a concentration far below the lower flammability limit or the toxic concentration. Furthermore, the ignition energy required is quite large. However ammonia is not suited to use in domestic refrigerators as the compressors are too large.

5.2 Alternatives for R114

The refrigerant R114, which boils at 4°C, is used as a refrigerant in a temperature domain between the one occupied by R12 (-30°C) and that occupied by R11 (24°C). It is non-flammable and almost non-toxic. However, as with R12, its effect on the environment is significant: it has an ODP equal to that of R12.

Only two refrigerants are cited as non-flammable, non-toxic alternatives. **R124a** (10°C/12°C) has a smaller ODP than R114 (0.02 compared with 1), but is still ozone depleting. It is acceptable as a transitional refrigerant, although it does not offer a definitive solution to the CFC problem. **R227** is regarded as a better alternative. It has an HGWP of 0.7 and good toxicological properties: the NOEL has been estimated at 50,000 ppm and, of all the laboratory animals exposed at 11 vol % over a four-hour period, none died. The COP is lower than that of R114, but the pressure ratio is better and the temperature increase during compression is less [49].

Current literature contains no information about flammable alternatives for R114.

5.3 Alternatives for R11

R11, being non-flammable, almost non-toxic and boiling at 24°C, is often used as a working fluid in heat pumps. As with R12 and R114, its ODP is 1. Generally speaking, the alternatives for R11 are more toxic than those for R12. Indeed, there is some positive relationship between boiling point and toxicity [50]. This makes the search for alternatives less easy. The literature only discusses R123 and its mixtures as alternatives.

R123 depletes the ozone layer, although not as much as R11. Many toxicological tests have been completed [51], showing a small acute toxicity. Exposure of rats for 28 or 90 days caused a decrease in body weight and dilatation of the liver. There were no indications of teratogenity or mutagenity.
A number of male rats, exposed to 5000 ppm, developed some non-virulent tumours. For that reason, Du Pont lowered its AEL-value to 10 ppm. Allied Signal even propose 5 ppm for a 40-hour working week [52]. The power consumption of the refrigeration system is about 10% higher than with R11. R123 can also damage the windings of an electric motor and it is not applicable in combination with usual lubricants and packings [39, 40].

A mixture of **R123** and the flammable **R141b** (32°C) has also been proposed [53]. Its aim is to diminish the high level of toxicity and HGWP and the non-zero ODP of R123 by mixing this refrigerant with R141b. In our opinion, this seems to be the best alternative to R11.

5.4 Conclusion

The most appropriate non-flammable alternatives to R12, R114 and R11 are R134a, R227 and R123, respectively. However, in order to obtain lower HGWP values, non-flammable mixtures of flammable and non-flammable refrigerants can also be considered. Relevant flammable alternatives are ammonia and propane. However, because of their inherent safety risks, adequate precautions have to be taken when systems operating with these fluids are designed.

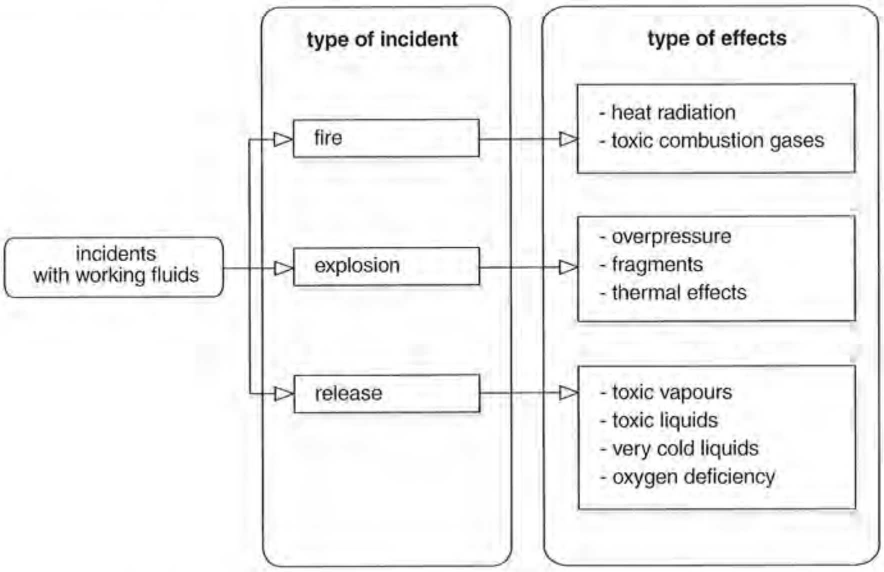
PART TWO

HAZARD EVALUATION AND ACCIDENT ASSESSMENT

6. HAZARD IDENTIFICATION AFTER AN ACCIDENT

The main types of incident involving working fluids in heat pumps and refrigeration equipment, and the associated hazards, are shown in Figure 6.1.

Figure 6.1 Working fluids: schematic overview of incidents and effects



The most important hazards that must be taken into account are listed below.

• Fire	effects of heat radiation
• Explosion	effects of overpressure impact of fragments thermal effects
• Intoxication	inhalation of toxic working fluid vapours inhalation of combustion products (fire) ingestion of toxic working fluids external contact with toxic working fluids
• Asphyxiation	
• Freezing	

A more detailed description of each of these hazards is given below. Only the effects on people are considered.

6.1 Fire

Ignition of a flammable working fluid gives rise to a fire posing a hazard to persons in its neighbourhood. This hazard may be associated with direct flame impact as well as with exposure to the heat radiated.

Different types of fire can be distinguished.

- Jet flame The ignition of a continuous release of a flammable working fluid from an orifice
- Pool fire The ignition of a pool formed after the liquid release of a flammable working fluid
- Fire-ball When a vessel containing a liquefied working fluid (under pressure) suddenly fails and the expanding boiling (and flammable) liquid is ignited
- Flash fire The ignition of a flammable vapour cloud resulting in the burning of that cloud without any build-up of pressure

Each type of fire requires, in the first instance, a flammable working fluid and an ignition source. The phase of the released working fluid is also important in relation to the spread or dispersion of the flammable substance. For the gas phase, dangerous concentrations can be expected at greater distances from the source of release than for the liquid phase.

The total amount of flammable working fluid in the installation will limit the maximum energy release for combustion. A higher working pressure in the installation reduces the time required to set this total amount free.

6.2 Explosion

A distinction can be made between two types of explosion:

- mechanical explosions;
- chemical explosions.

6.2.1 Mechanical explosions

During a mechanical explosion a pressurised fluid is suddenly released, giving rise to pressure waves. Fragments of the vessel, when combined with this pressure wave, may be turned into missiles. Both pressure waves and fragments may cause damage to the surrounding environment. Emphasis is on the *sudden* release of the vessel's contents. In the case of a small leak involving continuous fluid release, neither pressure waves nor fragments are to be expected.

A further distinction can be made according to the phase of the working fluid at the moment of release.

- If compressed gas is suddenly released, a pressure wave may be generated by the expansion of the gas. The amount of expansion energy is determined by the volume of the expanding gas and by its pressure before and after release.

- If a liquefied working fluid is suddenly released at a temperature above the atmospheric boiling point of the fluid, a pressure wave is generated by the expansion of the boiling liquid. This is a boiling liquid expanding vapour explosion (BLEVE). The expansion energy is a function of the volume of the liquid phase in the vessel and the degree to which it is overheated. The latter can be defined as the difference between the temperature of the liquid at the moment of release and the atmospheric boiling point of the working fluid.

Both types of explosion are classified as mechanical.

6.2.2 Chemical explosions

Chemical explosions involving working fluid vapours are usually reactions of the combustion type. When a flammable working fluid is accidentally released, a flammable cloud may ensue which may, in turn, give rise to a chemical explosion. This type of explosion may result in damage both from vessel fragmentation and from pressure waves. In addition, a fire hazard is created during the explosion. If the combustion cloud burns without any pressure effects (flash fire), only the thermal effects of the fire hazard are present.

A chemical explosion of the combustion type is only possible if a flammable working fluid forms a gas-air mixture with a concentration between the lower explosive limit (LEL) and the upper explosive limit (UEL). Furthermore, an ignition source must be present to initiate the combustion process. The energy delivered must be greater than the minimum ignition energy which is a property of the flammable working fluid.

An important distinction can be made between explosions involving an unconfined flammable vapour cloud and those where the cloud is confined.

- An unconfined vapour cloud explosion (UVCE) will only generate a pressure rise during combustion if at least several hundred kg of explosive vapour is found within the cloud. If no pressure waves are generated a flash fire occurs and the only effects are likely to be thermal.

- If the explosion of a flammable cloud occurs in a confined space, overpressures of several bars (maximum 10 bar) may be generated, assuming that the initial pressure is atmospheric and the room remains intact.

The important properties of the working fluids with respect to chemical explosions of the combustion type are the LEL, UEL, minimum ignition energy, heat of combustion and density of the vapour. As already indicated, the degree of confinement of the flammable mixture is also very important.

6.3 Intoxication

Intoxication can occur by:
- inhalation;
- ingestion;
- external contact.

The main mode of exposure in the case of an accidental working fluid release involves inhalation.

6.3.1 Inhalation

Intoxication by inhalation may occur when the working fluid gives rise to toxic vapours. A distinction can be made between two types of exposure:

- a long exposure to low concentration;
- a brief exposure to high (lethal) concentrations.

For a long exposure to low concentrations, different limits are used, for example the Threshold Limit Value (TLV). This is the airborne concentration of a substance corresponding to the conditions to which it is believed all workers may normally be exposed over a working lifetime without adverse effects. This kind of limit is not applicable to accidental working fluid releases.

For a brief exposure to high concentrations the relevant property is the acute inhalation toxicity of the working fluid. This can be expressed as, for example, the LC_{50} value, the lethal concentration that will result in the death of 50% of the population after a given period of exposure. This lethal concentration is given as the concentration of the working fluid in the inhaled air (mg/l or ppm), together with the corresponding exposure time.

Only the latter type of exposure will be examined within the context of this report.
The danger of brief exposure to high concentrations of toxic vapours can derive from two sources:

- toxic working fluid vapours;
- toxic decomposition products.

Apart from the lethal concentration which is a property of the working fluid itself, it is clear that other properties of the working fluid as well as the kind of accident and the type of release play a role in the formation of toxic vapours. Important factors include:

- amount released (continuous or instantaneous)
- vapour pressure of the fluid released;
- temperature of the fluid released;
- density of the vapour;
- dispersion situation;
- exposure time.

Furthermore, in a fire, toxic combustion gases may be formed. The important factors that need to be considered under such circumstances include:

- kind of toxic gases formed;
- formation rate of toxic combustion gases;
- dispersion situation.

Information on accidents with working fluids reveals that toxic combustion gases are also formed as a result of the decomposition of other substances in the fire, e.g. isolation materials.

6.3.2 Ingestion

For ingestion, the relevant property of the working fluid is its acute oral toxicity, expressed as the LD_{50}, the lethal dose that will result in the death of 50% of the population. This lethal dose is given as the absorbed quantity (mg) of the toxic fluid per kg body weight. This type of exposure is very unlikely to occur and is not considered further in this report.

6.3.3 External contact

Negative effects resulting from external contact with the working fluid are expressed in terms of the acute dermal toxicity, i.e. the LD_{50}. This lethal dose is given as the amount applied to the skin (mg) per kg body weight. This type of exposure is more likely to occur than ingestion, but only if personnel are very close to the installation at the time of the accident (e.g. during maintenance). Intoxication by external contact will not be considered further in this report.

6.4 Asphyxiation

Asphyxiation may occur when the working fluid gives rise to vapours that do not maintain the transport of oxygen to the lungs. As for the inhalation of toxic vapours, the properties of the working fluid as well as the kind of accident and the type of release play a role in expelling the air (and oxygen). The important factors involved are similar to those for the inhalation of toxic vapours (Section 6.3.1).

6.5 Freezing

Very cold working fluids may give rise to freeze burns on contact with the human skin. They may also result in metal embrittlement after contact with metal surfaces.

7. INDICES AS A MEANS OF HAZARD EVALUATION

One technique for evaluating the various hazards involves the use of hazard indices. Of the relevant techniques which have been developed in the past, the DOW Chemical Company's Fire and Explosion Index (F&EI) is almost certainly the most widely used for determining the effects of fires and explosions. It is based on statistical loss data. The Index is publicly available and has already passed through six editions: it is therefore considered to be suitable for calculating hazard indices for installations incorporating working fluids, at least with respect to the effects of fire and explosions.

The DOW Fire and Explosion Index also allows calculation of a Toxicity Index. Different indices are given, allowing working fluids to be classified on the basis of their toxic properties.

No indices are available for the remaining hazards, i.e. asphyxiation and freezing. The main reason is probably that these hazards can always be expected to occur very close to the installation. Furthermore, if the working fluid involved is flammable and/or toxic, the flammability hazards will extend beyond those where asphyxiation and freezing are likely to occur.

7.1 DOW Fire and Explosion Index

The DOW Chemical Company's Fire and Explosion Index is described in the company's 'Fire and Explosion Index, Hazard Classification Guide' [54]. The Guide was originally published in 1964. The sixth edition will be considered in this report.

The Index is a general technique for evaluating the fire, explosion and reactivity potential of process equipment and its contents. Using the F&EI system it is possible to quantify the expected damage of potential fires and explosions and to identify the equipment that would be likely to contribute to the escalation of an incident. It is important to note that the Index is determined separately for any process unit that can readily be identified as a separate entity, and for any primary item of process equipment. Furthermore, each different state of operation has to be considered separately during index calculation.

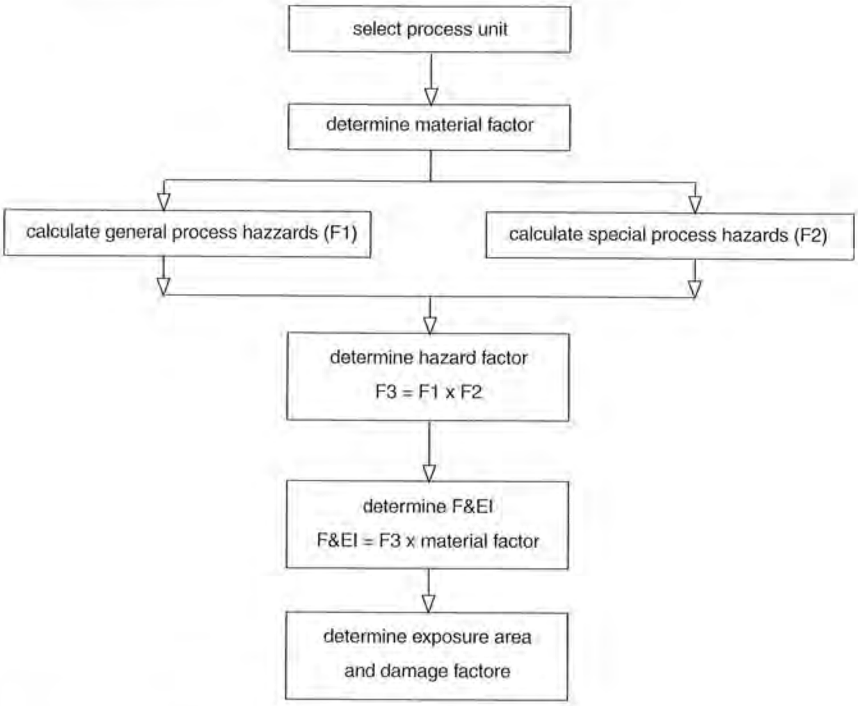
Quantification of the expected damage is based on historic loss data obtained from accidents of a certain magnitude: a minimum amount of flammable, combustible or reactive material therefore has to be incorporated in the process unit to produce a realistic estimate of the expected damage. Identification of the different factors that can contribute to an accident can also be used for smaller units. The predicted damage will, however, be overestimated.

The F&EI calculation is based on three important parameters:

- the material factor, which quantifies the possible fire and explosion hazards of the working fluid itself;
- general process hazards - the contributory hazards that play a primary role in determining the scale of a loss accident;
- special process hazards - the hazards that contribute primarily to the probability of a loss accident occurring.

These three parameters are further discussed below, and an overview of the calculation procedure is given in Figure 7.1. The values obtained during calculation should be entered into an appropriate schema, as shown in Figure 7.2 at the end of this chapter.

Figure 7.1 Schematic calculation procedure for DOW F&EI



7.1.1 The material factor

The material factor is a measure of the intrinsic potential for energy release during a fire or explosion of the substance under consideration. It is the basic starting value in the computation of the F&EI. The material factor is expressed as a number in the 1-40 range and is determined on the basis of only two properties: flammability and reactivity.

Listed substances

The material factor for many listed substances may be found using a classification developed by the NFPA which takes into account flammability and reactivity (or instability). Flammability is expressed by the flammability value (N_f) and reactivity by the reactivity value (N_r). The relevant values for a number of working fluids are given in Table 2.1.

Table 7.1 Overview classification of certain flammable working fluids according to NFPA

Working fluid		N_f	N_r
Ethylene	(R1150)	4	2
Propene	(R1270)	4	1
Propane	(R290)	4	0
Butane	(R600)	4	0
Chloromethane	(R40)	4	0
Dichloroethane	(R1130)	3	2
Ethane	(R170)	4	0
Ammonia	(R717)	1	0
Methane	(R50)	4	0

Unlisted fluids

Equivalent values can be determined for fluids not listed in NFPA (325M or 49) using the procedure outlined below.

The reactivity value[1] can be obtained from a qualitative description of the instability (or reactivity with water) of the working fluid or mixture at ambient temperature according to the following scale:

$N_r = 0$ Fluid is completely stable, even when heated under fire conditions
$N_r = 1$ Mild reactivity upon heating under pressure
$N_r = 2$ Significant reactivity, even without heating or pressure
$N_r = 3$ Detonation possible with confinement
$N_r = 4$ Detonation possible without confinement

A few exceptions to the above classification and an alternative and more objective method for determining the reactivity can be found in the Fire and Explosion Index Hazard Classification Guide. In this context, however, the description given above is adequate.

The flammability value for liquids and gases can be obtained from the NFPA classification outlined below.

$N_f = 0$ Non-combustible[2]
$N_f = 1$ Flash point[3] > 93.3°C (200°F)
$N_f = 2$ Flash point ≥ 37.8°C (100°F) and < 93.3°C (200°F)
$N_f = 3$ Flash point < 37.8°C (100°F) and boiling point[4] ≥ 37.8°C
$N_f = 4$ Flash point < 22.8°C (73°F) and boiling point < 37.8°C (100°F)

The material factor is a combination of reactivity and flammability values and can be determined from Table 7.2. It can be used to generate a first classification of working fluids regarding the possible effects of fire and explosion.

Table 7.2 Determination of the material factor

Flammability or combustibility	**Reactivity and instability**				
	$N_r = 0$	**$N_r = 1$**	**$N_r = 2$**	**$N_r = 3$**	**$N_r = 4$**
Nf = 0	1	14	24	29	40
Nf = 1	4	14	24	29	40
Nf = 2	10	14	24	29	40
Nf = 3	16	16	24	29	40
Nf = 4	21	21	24	29	40

---

[1] Reactivity includes self-reactivity (instability) and reactivity with water
[2] Will not burn in air when exposed to a temperature of 815°C for a period of five minutes
[3] Closed cup flash point
[4] Boiling point at standard temperature and pressure

The most dangerous working fluids with respect to fire hazards have an N_f value of 3 or 4. Depending of the reactivity (N_r), the material factor will then be between 16 and 24 although one fluid, tetrafluoroethylene, has a material factor of 29. Typical working fluids and their material factor are given in Table 7.3. The value for ammonia is low because the gas is difficult to ignite.

According to the national standards, those working fluids that pose a danger with respect to fire and explosion cannot generally be used in domestic situations or in rooms where people are present. They are normally to be found only in industrial installations.

Adjustments to the material factor

It is important to recognise that the material factor represents the hazard of the selected material at ambient temperature and pressure. The effect of overpressure or underpressure is taken into account when assessing the 'special process hazards'. If, however, the temperature is > 60°C (140°F), the material factor will require adjustment as follows:

Table 7.3 Material factors according to DOW guide

Working fluid		Material factor
Ethylene	(R1150)	24
Propene	(R1270)	21
Propane	(R290)	21
Butane	(R600)	21
Chloromethane	(R40)	21
Dichloroethane	(R1130)	24
Ethane	(R170)	21
Ammonia	(R717)	4
Methane	(R50)	21

- if the temperature is above the flash point, 1 has to be added to the flammability value (with a maximum of 4);
- if the temperature is above exotherm start[1], or auto-ignition, 1 has to be added to the reactivity value (with a maximum of 4).

No temperature adjustment has been included in Table 7.3.

7.1.2 General process hazards

As mentioned before, the so-called general process hazards play a primary role in determining the magnitude of loss during an accident. By assigning penalties to dangerous process conditions/situations, these hazards can be quantified.

An overview of the dangerous process situations is given below, but only those hazards that are meaningful within the context of this report will be examined in detail.

---

[1] Temperature at which a heat-generating chemical reaction is first detected in acceleration rate calorimetry or a similar calorimeter

Exothermal chemical reaction

Only applicable if the process unit is a reactor.

Endothermal processes

Only applicable if the process unit is a reactor.

Materials handling and transfer

Only applicable to the handling, transfer and warehousing of materials.

Enclosed or indoor process units

The processing of flammable liquids and gases in open and freely ventilated constructions will permit the rapid dissipation of any vapours released, thereby reducing the explosion potential. Even properly designed mechanical ventilation is not as effective as an open construction, but if a mechanically ventilated system is designed in such a way that all flammables are collected and dispersed, the penalty can be reduced.

An enclosed area is defined either as any roofed area with three or more sides, or as an area enclosed by a roofless structure with walls on all sides. The penalties applied are outlined below.

1. Any process in which flammable liquids are handled at temperatures above their flash point in an enclosed area incurs a penalty of 0.30. For quantities in excess of 4500 kg (10,000 lb) or ≈ 3800 l (1000 gallons), a penalty of 0.45 is used.
2. Any process in which liquefied petroleum gas (LPG) or any flammable liquids are handled at temperatures above their boiling point within an enclosed area is given a penalty of 0.60. For quantities in excess of 4500 kg (10,000 lb) or ≈ 3800 l (1000 gallons), a penalty of 0.90 is used. Where properly designed mechanical ventilation is installed, these penalties may be reduced by 50%.

Access

Emergency equipment must have ready access to the area housing the process unit. Access from at least two sides is considered to be the minimum requirement. A penalty of 0.35 is applied to all process areas over 925 m^2 not having adequate access. For smaller areas judgement must be used in assessing the access requirements. A penalty of 0.2 can be applied if sound engineering judgement indicates a potential for fire control problems as a result of inadequate access.

Drainage and spill control

As inadequately designed drainage has been a contributory factor in a large number of losses involving liquid spills, penalties are applied where design conditions could cause large spills of flammable or combustible material to be retained around or near the process equipment.

The penalties outlined below are only applied if the material in the process unit has a flash point < 60°C (140°F).

1. Diking which is designed to prevent a spill from expanding to other areas but which exposes all the equipment within the dike incurs a penalty of 0.50.
2. A flat area around the process unit which allows spills to spread, exposing large areas to fire if ignited, incurs a penalty of 0.50.

3. A diking design that surrounds three sides of an area and directs spills to an impounding basin or non-exposing drainage trench incurs no penalty if the following criteria are met:

   - the slope to the basin or trench is a minimum of 2% for earthen surfaces, or 1% for a hard surface;
   - the distance to the equipment from the nearest edge of the trench or basin is at least 8 m (25 ft);
   - the impounding basin has a capacity of at least 75% of the process unit's capacity plus a 30-minute flow rate of fire fighting water.

   If the above criteria are partially met, a penalty of 0.25 may be applied. If the basin or trench exposes utility lines or does not meet the distance requirements, a penalty of 0.50 is applied. It can be concluded from the above that excellent drainage is required if penalties are to be avoided.

The general process hazards factor can be calculated by adding all the penalties found and adding this total to the base factor of 1.00.

7.1.3 Special process hazards

As noted above, the so-called special process hazards contribute primarily to the probability of a loss accident. The technique for quantifying these hazards is the same as that for the general process hazards, i.e. giving penalties to specific process conditions/situations that have shown themselves to be major causes of fire and explosion incidents. Only those hazards that are meaningful within the context of this report will be examined in detail.

Toxic materials

A penalty is applied for toxic materials that may complicate the response of emergency personnel, thereby reducing their ability to investigate or mitigate damage during an incident.

This penalty is based on the health factor (N_h) as defined in NFPA 704 (or given in NFPA 325M or 49):

$N_h = 0$ No hazard beyond that of ordinary combustibles
$N_h = 1$ Only minor residual injury likely
$N_h = 2$ Prompt medical attention required to avoid temporary incapacitation
$N_h = 3$ Materials causing serious temporary or residual injury
$N_h = 4$ Short exposure causes death or major injury

The health factors for various working fluids are given in Table 7.4.

Table 7.4 Health factors for various working fluids according to NFPA

Working fluid		N_h
Ethylene	(R1150)	1
Propene	(R1270)	1
Propane	(R290)	1
Butane	(R600)	1
Ammonia	(R717)	3
Sulphur dioxide	(R764)	3
Dichloromethane	(R30)	2
Chloromethane	(R40)	2
Dichloroethane	(R1130)	2
Ethane	(R170)	1
Methane	(R50)	0

The penalty applied is 0.2 x N_h. It must be clear that the applied penalty is intended to represent the emergency limitations which can cause additional loss. The intoxication of people near the process unit is not part of the emergency and personnel factors are not therefore taken into account. This is quite logical as the hazard index being formulated is a *fire* and *explosion* index.

Sub-atmospheric pressure

This penalty applies to a process condition where air leakage in a system could create a hazard either from the contact of air with moisture-sensitive or oxygen-sensitive materials, or from the formation of flammable mixtures on the introduction of air.

The penalty is only applied if the absolute pressure is < 500 mm Hg. If this penalty is applied, the following two penalties should not.

Operation in or near the flammable range

Certain operating conditions which can allow air to enter and be retained within the system could lead to the formation of a flammable mixture, thereby creating a hazard.

1. Process equipment or process storage tanks that would be in or near the flammable range only in the event of instrument or equipment failure incur a penalty of 0.30.
2. Processes or operations that naturally occur in or near the flammable range because purging is either impractical or not selected as an option incur a penalty of 0.80.

Relief pressure

Where the operating pressure is above atmospheric pressure, a penalty is applied to take into account the effect of high pressure on the potential for leaks and the associated high release rates. The concern here is for the possible failure of some component in the process unit, causing the release of flammable materials.

The guide for the F&EI includes a curve, allowing the penalty to be determined as a function of the pressure. The penalty can also be determined by calculation, using the following formula:

$$\text{penalty} = \frac{a + c.x}{1 + b.x} \qquad 0 < x < 70 \quad (7.1)$$

where:

x = pressure (barg)
$a = 0.1536$
$b = 0.0233$
$c = 0.0302$

The formula applies only to flammable and combustible liquids with a flash point of <60°C (140°F).
Pressure is determined using the following procedure:

1. Find the penalty using the formula given above, taking into account the operating pressure.
2. If the material involved is a compressed gas, the penalty found in Step 1 has to be adjusted by multiplying by 1.2.
   If the material is a liquefied flammable gas (or other flammable material stored above its boiling point), the penalty should be multiplied by 1.3.
3. Substituting the relief pressure (or rupture disk pressure) in formula 7.1, determine the relief pressure penalty.

The actual penalty applied is then found by multiplying the adjusted penalty established in Step 2 by the ratio of the operating pressure penalty (Step 1) to the relief pressure penalty.

Low temperature
This penalty makes allowance for the possible brittleness of carbon steel or other metals that may be exposed to temperatures at or below their ductile/brittle transition temperatures. If a careful evaluation has been made and there is no possibility of temperatures below the transition temperature occurring under either normal or abnormal operating conditions, no penalty is applied.

Where the possibility of low temperatures does exist, the following penalties are applied:

1. The use of carbon steel combined with operation at or below the ductile/brittle transition temperature incurs a penalty of 0.30.
2. For materials other than carbon steel, where the operating temperature is at or below the transition temperature, a penalty of 0.20 is applied.

Quantity of flammable and unstable materials
As the quantities of flammable and unstable material in the process unit are increased, damage can be expected over a larger area if an accident occurs. Flammable materials might create a fire hazard. Unstable materials might, on exposure to fire, create a reactive chemical event.

A penalty is applied when the following materials are selected as working fluids:

- flammable liquids with a flash point of < 60°C (140°F);
- flammable gases;
- liquefied flammable gases;
- combustible liquids with a flash point > 60°C (140°F) when the process temperature is above the flash point;
- reactive materials, regardless of their flammability (N_r = 2, 3 or 4).

The next step is to determine the amount of material that might be released. Experience has shown that this can reasonably be estimated as either the quantity of material in the process unit under consideration or the quantity of material in the largest connected unit, whichever is the greater. Any connected unit that can be isolated by valves operable from a remote location during an emergency is removed from consideration.

The guide for the F&EI gives a curve allowing the penalty to be determined as a function of the product of the maximum amount of material released and the heat of combustion. The equivalent formula is:

$$\text{penalty} = a - \frac{b}{x} + \frac{c}{x} - \frac{d}{x^2} \qquad 0.1 < x < 100 \quad (7.2)$$

where:

$x = \text{penalty} = a - \frac{b}{x} + \frac{c}{x} - \frac{d}{x^2} \qquad 0.1 < x < 100 \quad (7.2)$

$a = 3.1799$

$b = 2.1499$

$c = 0.4339$

$d = 0.0057$

Corrosion and erosion

Although good design makes allowances for corrosion and erosion, some corrosion/erosion problems may still occur in certain processes. The corrosion rate is considered to be the sum of the external and internal corrosion rates. The following penalties apply:

1. Corrosion rate < 0.5 mm/year and risk of local erosion: penalty = 0.10
2. Corrosion rate ≥ 0.5 mm/year and < 1 mm/year: penalty = 0.20
3. Corrosion rate ≥ 1 mm/year: penalty = 0.50

Leakage - joints and packings

Gaskets, seals of joints or shafts, and packings can be sources of leaks for flammable material. The following penalties apply:

1. Where pump and gland seals are likely to result in some leakage of a minor nature: penalty = 0.10
2. For processes known to give regular leakage problems in pumps, compressors and flange joints: penalty = 0.20
3. For processes involving thermal and pressure cycling: penalty = 0.30
4. If the material in the process unit is penetrating in nature, or is an abrasive slurry that can cause intermittent sealing problems, and if the process unit uses a rotating shaft seal or packing: penalty = 0.40
5. Where a process unit has sight glasses, bellows assemblies or expansion joints: penalty = 1.50

Use of fired heaters

The presence of fired equipment in a process adds an additional probability of ignition when flammable liquids or vapours are released. A distinction is made between the release of the material above its flash point and the release of the material above its boiling point.

To determine the penalty it is necessary to know the distance from a probable emission point in the process unit to the fired heater's air intake.

Again, an equivalent equation for calculating the penalty in each case has been derived for the curves given in the F&EI guide.

$$\text{penalty} = \frac{a - c.x + e.x^2}{1 + b.x + d.x^2} \qquad \begin{cases} 0 < x < 65 \\ T_{\text{material}} \text{ above flash point} \end{cases} \qquad (7.3)$$

where:

x = distance between emission point and fired heater's air intake (m)
a = 0.9986
b = 0.0789
c = 0.0174
d = 0.0060
e = 0.0008

$$\text{penalty} = a - b.x.\sqrt{x} + c.x^2.\sqrt{x} - d.x^3 \qquad \begin{cases} 0 < x < 65 \\ T_{\text{material}} \text{ above flash point} \end{cases} \qquad (7.4)$$

where:

x = distance between emission point and fired heater's air intake (m)
a = 0.9891
b = 0.0093
c = 0.0003
d = 2×10^{-5}

Rotating equipment

Statistical evidence indicates that large pieces of rotating equipment (pumps and compressors) are likely to contribute to loss incidents.
A penalty of 0.50 is applied to process units that use (or are):

1. a compressor in excess of 600 hp;
2. a pump in excess of 75 hp.

The special process hazards factor can be calculated by adding all the penalties found and adding this total to the base factor of 1.00.

7.1.4 Calculating the Fire and Explosion Index

The product of the general process hazards factor and the special process hazards factor gives the unit hazard factor (Figure 7.2). The product of these factors rather than their sum is used because the contributing hazards are known to have a compounding effect.

The F&EI is then found as the product of the unit hazard factor and the material factor. It is used to estimate the damage that would probably result from an accident in the process unit. This damage is quantified in two ways.

- The radius of exposure in metres is found by multiplying the F&EI by 0.256. This indicates the area in which equipment could be exposed to the effects of fire and explosion in the process unit evaluated. It must, however, be clearly understood that, in reality, the effects do not spread over a perfect circle.
- The damage factor can be ascertained from curves given in the F&EI guide. It is determined from the material factor and the F&EI and represents the effects of fires and blasts.

A classification of the degree of hazard, according to the value of the F&EI, is given in Table 7.5.

Table 7.5 Degree of hazard as a function of the F&EI

F&EI	Degree of hazard
1-60	light
61-96	moderate
97-127	intermediate
128-158	heavy
>159	severe

The radius of exposure is only relevant if the amount of product in the evaluated process unit is sufficiently large (> ≈ 2.5 ton). Meaningful but overestimated results are obtained if the amount of product is at least 500 kg. If less product is involved, determining the penalties can still be worthwhile as an identification of the hazards. However, the degree of hazard as given in Table 7.5 is no longer appropriate, nor is the calculation of the exposure area.

7.1.5 Conclusion

As shown above, the F&EI makes it possible to quantify the possible effects of fires and explosions in a general way. It should be clear that the results obtained in this way are estimates of the possible effects based on the materials used in the process and the process conditions/installations. Different process units can be compared on the basis of their F&EI.

7.2 Toxicity Index

A toxicity index evaluates the toxic effects during an accident with a (toxic) working fluid. Its calculation is described in the fourth edition of the DOW F&EI guide and involves both a toxicity factor that takes into account the properties of the fluid (analogous to the material factor for the F&EI) and the hazards factors that take into account dangerous process conditions or situations.

7.2.1 The toxicity factor

The definition of the toxicity factor in the fourth edition of the DOW F&EI guide is based on the NFPA classification.

The health hazard is expressed by N_h[1]:

$N_h = 0$ No hazard beyond that of ordinary combustibles.

$N_h = 1$ Only minor residual injury likely. Includes materials that are moderate respiratory irritants or cause slight to moderate eye irritation or that give off irritating combustion products under fire conditions.

$N_h = 2$ Prompt medical attention required to avoid temporary incapacitation. Includes materials that cause severe but reversible respiratory, skin or eye irritation or give off toxic or highly irritating combustion products.

$N_h = 3$ Materials causing serious temporary or residual injury. Includes materials that are either severely corrosive to skin or cause irreversible eye damage or give off highly toxic combustion products.

$N_h = 4$ Short exposure causes death or major injury. Materials that, under normal or fire conditions, are extremely hazardous (toxic or corrosive) through inhalation or contact with or absorption by the skin.

The effects taken into account when determining the degree of hazard are listed below.

- Health hazards arising from an inherent toxic property of the (working) fluid or its products of decomposition or combustion. (For the health hazard rating only the inherent physical and toxic properties of the material are considered unless the combustion or decomposition products present a significantly greater degree of risk.)
- Health hazards resulting from a fire or other emergency condition that involves acute short-term exposure to a concentration of a hazardous material. Exposure time may range from a few seconds to one hour.
- Acute exposure by contact, inhalation or ingestion. (The oral route of exposure (ingestion) is highly unlikely under the conditions anticipated by this NFPA standard.)

A more detailed, quantitative description of the classification based on toxic properties is given in Table 7.6.

Table 7.6 Health hazard classification based on toxic properties (NFPA)

	Oral toxicity LD_{50} (mg/kg)	**Dermal toxicity LD_{50} (mg/kg)**	**Dusts and mists LC_{50} (mg/l)**	**Gases and vapours LC_{50} (ppm)**
$N_h = 0$	> 2000	> 2000	> 200	> 10,000
$N_h = 1$	> 500	> 1000	> 10	> 5000
	< 2000	< 2000	< 200	< 10,000
$N_h = 2$	> 50	> 200	> 2	> 3000
	< 500	< 1000	< 10	< 5000
$N_h = 3$	> 5	> 40	> 0.5	> 1000
	< 50	< 200	< 2	< 3000
$N_h = 4$	< 5	< 40	< 0.5	< 1000

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[1] The definition of this NFPA classification can be found in NFPA 704

The vapour pressure is also taken into account in determining the degree of hazard.

$N_h = 2$ Any liquid whose saturated vapour concentration at 20°C $\geq LC_{50}/5$ for acute inhalation toxicity and $LC_{50} \leq 5000$ ppm (and not meeting the criteria for degree 3 or 4).

$N_h = 3$ Any liquid whose saturated vapour concentration at 20°C $\geq LC_{50}$ for acute inhalation toxicity and $LC_{50} \leq 3000$ ppm (and not meeting the criteria for degree 4).

$N_h = 4$ Any liquid whose saturated vapour concentration at 20°C $\geq LC_{50}$ x 10 for acute inhalation toxicity and $LC_{50} \leq 1000$ ppm.

In calculating the toxicity factor according to the DOW guide, the required T_h factor is obtained from the NFPA degree of health hazard as shown in Table 7.7.

Table 7.7 The T_h factor as a function of the N_h value

N_h	T_h
0	0
1	50
2	125
3	250
4	325

In some cases the TLV is not consistent with the NFPA rating. To obtain the toxicity factor in such a case, a correction to the T_h value is required as shown in Table 7.8.

Table 7.8 Adjusting the T_h value with respect to the TLV

TLV	**Add to T_h**
≤ 5 ppm	125
> 5 and ≤ 50 ppm	75
> 50 ppm	50

The toxicity factor (TF) is then found by dividing the corrected T_h value by 100 ($TF=T_h/100$). The TF is a value in the 0-4.5 range. Table 7.9 gives the toxicity factor for a number of fluids.

Table 7.9 Toxicity factors according to the DOW guide

Working fluid		**TF**
Ethylene	(R1150)	1
Propene	(R1270)	1
Propane	(R290)	1
Butane	(R600)	1
Ammonia	(R717)	3.25
Sulphur dioxide	(R764)	3.75
Dichloromethane		(R30) 1.75
Chloromethane	(R40)	2
Dichloroethane	(R1130)	1.75
Ethane	(R170)	1
Methane	(R50)	0

In addition to the NFPA rating for toxic hazards and the toxicity factor derived according to the DOW guide, a number of other hazard factors have been developed.These include [55]:

- the Vapour Hazard Index (VHI);
- the Substance Hazard Index (SHI);
- the Adjusted Substance Hazard Indices (ASHI).

The VHI can be defined as:

$$\text{VHI} = \log\,(10^6 \times \text{atmospheric vapour pressure/TLV (ppm)})$$

The SHI is defined in a similar way: however, the log function is not present, and the reference limit (denominator) is an acute toxic concentration for which several values might be used.

If the TLV is used, the SHI is equivalent to the VHI. Using alternatives to the TLV to give an adjusted SHI allows:

- the use of different limits for the occupational exposure limit: the SHI is then adjusted as a function of the exposure limit used;
- skin absorption to be taken into account.

For example, for accidental releases, an acute toxic concentration such as the Short-Term Exposure Limit (STEL), the Immediately Dangerous to Life and Health (IDLH) values, or the LC_{50} values better reflect the acute chemical toxicity and are thus more relevant than, for instance, the TLV. STEL and IDLH values are not, however, always available.

The alternative toxic hazard indices defined above take two properties of the fluid into account: its vapour pressure and its acute toxicity limit.

- The vapour pressure is taken at ambient temperature (21°C/70°F). For gases the vapour pressure is taken at one atmosphere (not the saturation pressure at ambient temperature). It must be clear, however, that the temperature of the fluid at the moment of release is also important with respect to the vapour pressure. Adjusting the toxicity factor can also be necessary (as for the NFPA flammability value in the DOW guide). This can be achieved by taking the vapour pressure that corresponds to the temperature of the working fluid.

- In most cases an occupational exposure limit is used to determine the toxicity factor. It is clear, however, that this takes into account mainly intoxication by inhalation. In the case of accidental releases acute toxicity limits are to be preferred. One problem is that these limits are not available for all toxic substances. However, the available LC_{50} values could appropriately be used.

The toxicity factors derived do not take into account the vapour density of the toxic substance. This density plays an important role with respect to the initial dispersion of the toxic gas. The acute toxic limits are, however, mostly relatively low concentrations reached after considerable dilution. Dispersion at these concentrations will be determined mainly by the atmospheric turbulence. This implies a Gaussian dispersion that is independent of the density of the gas. Differences in dispersion behaviour can therefore only be expected at higher concentrations, i.e. near the source of release. The temperature of the released vapour also has a bearing on its density, a phenomenon that can be important near the source of the release.

A limited classification of the main toxic refrigerants for which the different toxicity factors were found is given in Table 7.10. This includes, as well as the Vapour Hazard Index, an analogous index calculated using the LC_{50} value (for rats: 1 hour exposure). The rankings based on N_h, TF and VHI agree fairly well. However, as the LC_{50} value can differ as a function of the source, the final column should only be regarded as an approximation.

7.2.2 Calculating the Toxicity Index

A similar procedure is used for calculating the Toxicity Index as for deriving the F&E Index. The toxicity factor (TF) is multiplied by the sum of the general process hazards factor (F_1), the special process hazards factor (F_2) and a value of 2 (Figure 7.2).

In contrast to the F&EI, the Toxicity Index is only valid for comparisons between installations. It gives no information about the area of exposure or the degree of hazard. For these calculations, specific effect evaluation is necessary (Chapter 9).

Table 7.10 Limited classification of toxic working fluids

Refrigerant		**N_h (NFPA)**	**TF**	**VHI**	**Log (10^6 vap. press (atm)/ LC_{50} (ppm))**
Sulphur dioxide	(R764)	3	3.75	5.7	2.59
Ammonia	(R717)	3	3.25	4.6	2.31
Chloromethane	(R40)	2	2	4.3	1.28
Dichloroethane	(R1130)	2	1.75	3.24	–
Ethyl chloride	(R160)	2	1.75	3	–
Dichloromethane	(R30)	2	1.75	2.94	1.40

Calculation of Fire & Explosion Index and Toxicity Index		
Process unit		
Working fluid in process unit	Material factor	
State of operation		
GENERAL PROCESS HAZARDS		penalty
base factor		1.00
• enclosed or indoor process unit		
• access		
• drainage and spill control		
General process hazards (F1)		
SPECIAL PROCESS HAZARDS		
base factor		1.00
• toxic materials		
• sub-atmospheric pressure		
• operation in or near flammable range		
• relief pressure		
• low temperature		
• quantity of flammable and unstable materials		
• corrosion and erosion		
• leakage - joints and packings		
• use of fired heaters		
• rotating equipment		
Special process hazards (F2)		
Unit hazard factor (F3 = F1 x F2)		
Fire & Explosion index (F&EI = F3 x MF)		
toxicity factor (TF = T_h/100)		
Toxicity Index (TI = TF x (F_1 + F_2 + 2))		

Figure 7.2 Calculation schema: Fire & Explosion Index and Toxicity Index

7.3 Conclusion

The information presented in this chapter suggests an obvious division of working fluids into three categories:

- those working fluids that present mainly fire and explosion hazards;
- toxic working fluids;
- those working fluids that pose no significant hazards with respect to fire and explosion and which do not give rise to toxic concentrations.

In the first instance, the material factor and the F&EI can be used to classify, respectively, the working fluids and the installations in which they are used. The F&EI also provides a tool for estimating the areas over which the fires and explosions have an impact.

In the case of toxic working fluids, the toxicity factors and the Toxicity Index can be used to classify, respectively, the working fluids and the installations in which they are applied.

Where working fluids pose no significant fire, explosion or toxicity hazards, the most likely effects are asphyxiation, freezing and, depending on the composition of the working fluid, the generation of toxic combustion gases. No general techniques exist for evaluating these effects.

This classification of working fluids is similar to the division into Groups 1, 2 and 3 applied in most of the standards (Annex 1). For those fluids in Group 3 the F&EI is applicable. For those in Group 2, toxicity factors and the Toxicity Index apply.

8. APPLYING INDICES TO AN INDUSTRIAL INSTALLATION

The application which follows assumes an industrial installation using ethylene and ammonia. The industrial process considered requires very low temperatures which are achieved by using ethylene as the working fluid. The condensation of the ethylene occurs at low temperatures, and a second refrigeration cycle using ammonia is therefore present.

8.1 Calculating the Fire and Explosion Index

The application calculates the F&EI for:

- the process storage of ethylene in one of four vessels, each of which contains about 9.5 tons of ethylene;
- the 8 MW ethylene compressor;
- the process storage of ammonia in one of two vessels, each of which contains about 17 tons of ammonia.

The application demonstrates that only a minimum of information is required to evaluate these installations using the F&E Index.

8.1.1 Ethylene process storage

Material factor

The material factor for ethylene is 24. The liquefied ethylene is at a temperature of approximately -20°C and saturation pressure. Because the temperature is below 60°C no adjustment of the material factor is required.

General process hazards

The relevant penalties are listed below.

- As the vessel is situated in the open air, no penalty is applied.
- As the access is good, no penalty is applied.
- The penalty for drainage and spill control is applicable because the material involved has a flash point below 60°C. The flat area around the vessel incurs a penalty of 0.5.

The general process hazards factor is found by adding the applied penalties to the base factor. In this case it totals 1.50 (Figure 8.1).

Special process hazards

The relevant penalties are listed below.

- Because $N_h = 1$, a toxic hazards penalty of 0.2 is applied.
- Because the saturation pressure is above atmospheric, no penalty is applied for sub-atmospheric pressure. Nor does the penalty for operation in the flammable range apply.
- The penalty for the relief pressure (applicable because the flash point is < 60°C) is calculated as follows:
  - using Formula 7.1 and the operating pressure of 26 barg gives a penalty of 0.58;
  - this penalty is multiplied by 1.3 as the material involved is a liquefied gas (0.58 x 1.3 = 0.75);
  - the revised penalty is adjusted by the ratio of the initial penalty (0.58) to the penalty for the relief pressure at 32 barg (0.64);
  - the final penalty applied is therefore 0.75 x (0.58/0.64) = 0.68.
- Good construction practice for the vessel is assumed, so no penalty for low temperature is applied.
- The penalty for the quantity of flammable material depends on the amount that can be released in an accident. For vessels containing a liquefied gas, the F&E Index is calculated for one vessel. If remote control valves are installed on the pipes interconnecting the four vessels, then the penalty per vessel is calculated using Formula 7.2. The input for this formula is found from:

  $$9500\ (\text{kg}) \times 48.4\ (\text{MJ/kg}) / 1.058 \times 10^6 = 0.43.$$

  The penalty is then equal to 0.88. If there are no remote control valves on the interconnecting pipework so that all the working fluid could be released from the four vessels, then the penalty. based on a total of 38,000 kg of fluid, is 1.8.
- Corrosion is not relevant, so no penalty is applied.
- As sight glasses are present a (severe) penalty of 1.50 is applied.
- As a fired heater is present at a distance of > 65 m, the minimum penalty is applied (0.1).
- The penalty for rotating equipment is not applicable.

The special process hazards factor is found by adding the applied penalties to the base factor. In this case, assuming the lower of the two penalties for the quantity of flammable material, it totals 4.36 (Figure 8.1).

Calculating the F&EI

The unit hazard factor (F3) and the F&EI are calculated as shown in Figure 8.1. Both values would be significantly higher if the higher penalty for the quantity of flammable material needed to be assumed (no remote controlled valves to isolate the vessels from each other). At the same time a significant reduction could be achieved by replacing the sight glasses. The effects of these changes are summarised in Table 8.1.

Figure 8.1 F&EI for the process storage of ethylene

Calculation of Fire & Explosion Index and Toxicity Index			
Process unit	refrigeration installation		
Working fluid in process unit	ethylene	Material factor	24
State of operation	process storage		
GENERAL PROCESS HAZARDS			penalty
base factor			1.00
• enclosed or indoor process unit			/
• access			/
• drainage and spill control			0.50
General process hazards (F1)			1.50
SPECIAL PROCESS HAZARDS			
base factor			1.00
• toxic materials			0.20
• sub-atmospheric pressure			/
• operation in or near flammable range			/
• relief pressure			0.68
• low temperature			/
• quantity of flammable and unstable materials			0.88
• corrosion and erosion			/
• leakage - joints and packing			1.50
• use of fired heaters			0.10
• rotating equipment			/
Special process hazards (F2)			4.36
Unit hazard factor (F3 = F1 x F2)			6.54
Fire & Explosion index (F&EI = F3 x MF)			157

Table 8.1 Influence of installation layout on the F&EI for the process storage of ethylene

Installation layout	F&EI	Degree of hazard	Radius of exposure
Sight glasses, no valves	190	Severe	49 m
Sight glasses, valves	157	Heavy	40 m
No sight glasses, valves	103	Intermediate	26 m

8.1.2 Ethylene compressor

Material factor

The material factor for ethylene is 24.

General process hazards

The relevant penalties are listed below.

- As the compressor is situated in the open air, no penalty is applied.
- No penalty is applied for access.
- The penalty for drainage and spill control is not applicable. In the case of a leak the ethylene would be released in its gas phase and the conditions of the area under the compressor would not be particularly important.

The general process hazards factor therefore remains at 1.0 (Figure 8.2).

Special process hazards

The relevant penalties are listed below.

- Because $N_h = 1$, a toxic hazards penalty of 0.2 is applied.
- Because the saturation pressure is above atmospheric, no penalty is applied for sub-atmospheric pressure.
- For operation in or near the flammable range, a penalty of 0.30 is applied as flammable vapours could be released in the case of process equipment failure.
- The penalty for the operating pressure is derived from Formula 7.1 where the maximum operating pressure is 26 barg. The penalty derived is multiplied by 1.2 for compressed gases, and the final penalty is 0.70.
- Good construction practice is assumed, so no penalty for low temperature is applied.
- The penalty for the quantity of flammable material depends on the amount that can be released in an accident. In this instance the amount released will be limited and the minimum penalty is applied. The input for Formula 7.2 is taken as 0.1, giving a final penalty of 0.16.
- A corrosion penalty of 0.10 is applied as there is a risk of local corrosion.
- For minor leaks a penalty of 0.10 is applied.
- As a fired heater is present at a distance of > 65 m, the minimum penalty is applied (0.1).
- For rotating equipment a penalty of 0.50 is applied.

The special process hazards factor in this case totals 3.16 (Figure 8.2).

Calculating the F&EI

The unit hazard factor (F3) and the F&EI are calculated as shown in Figure 8.2. The degree of hazard is moderate and the radius of exposure is equal to some 20 m.

Figure 8.2 F&EI for ethylene compressor

Calculation of Fire & Explosion Index and Toxicity Index			
Process unit	refrigeration installation		
Working fluid in process unit	ethylene	Material factor	24
State of operation	compressor		
GENERAL PROCESS HAZARDS			penalty
base factor			1.00
• enclosed or indoor process unit			/
• access			/
• drainage and spill control			/
General process hazards (F1)			1.00
SPECIAL PROCESS HAZARDS			
base factor			1.00
• toxic materials			0.20
• sub-atmospheric pressure			/
• operation in or near flammable range			0.30
• relief pressure			0.70
• low temperature			/
• quantity of flammable and unstable materials			0.16
• corrosion and erosion			0.10
• leakage - joints and packing			0.10
• use of fired heaters			0.10
• rotating equipment			0.50
Special process hazards (F2)			3.16
Unit hazard factor (F3 = F1 x F2)			3.16
Fire & Explosion index (F&EI = F3 x MF)			76

8.1.3 Ammonia process storage

Material factor

The material factor for ammonia is 4. The liquefied ammonia is at about 30°C (and saturation pressure). The temperature is below 60°C so no adjustment of the material factor is required.

General process hazards

The relevant penalties are listed below.

- As the vessel is situated in the open air, no penalty is applied.
- As the access is good, no penalty is applied.
- The flat area around the vessel gives rise to a penalty of 0.5.

The general process hazards factor in this case totals 1.5 (Figure 8.3).

Special process hazards

The relevant penalties are listed below.

- Because $N_h = 3$, a toxic hazards penalty of 0.6 is applied.

- Because the saturation pressure is above atmospheric, no penalty is applied for sub-atmospheric pressure. Nor does the penalty for operation in the flammable range apply.

- The penalty for the relief pressure (applicable because the flash point is < 60°C) is calculated as follows:
  - using Formula 7.1 and the operating pressure of 10 barg gives a penalty of 0.37;
  - this penalty is multiplied by 1.3 as the material involved is a liquefied gas (0.37 x 1.3 = 0.48);
  - the revised penalty is adjusted by the ratio of the initial penalty for the operating pressure (0.37) to the penalty for the relief pressure at 15 barg (0.45);
  - the final penalty applied is therefore 0.48 x (0.37/0.45) = 0.39.

- Good construction practice for the vessel is assumed, so no penalty for low temperature is applied.

- The penalty for the quantity of flammable material depends on the amount that can be released in an accident. For vessels containing a liquefied gas, the F&E Index is calculated for one vessel. Here the maximum amount that can be released is about 17 tons. Using Formula 7.2 the penalty is 0.64.

- Corrosion is not relevant, so no penalty is applied.

- No penalty is applied for leakage.

- As a fired heater is present at a distance of > 65 m, the minimum penalty is applied (0.1).

- The penalty for rotating equipment is not applicable.

It should be added that the penalties for flammable gases have been applied been conservatively applied, even though ammonia is hard to ignite.

The special process hazards factor in this case totals 2.73 (Figure 8.3).

Calculating the F&EI

The unit hazard factor (F3) and the F&EI are calculated as shown in Figure 8.3. It is clear that the very low value for the material factor results in a low F&EI. The degree of hazard is only light.

Figure 8.3 F&EI for the process storage of ammonia

Calculation of Fire & Explosion Index and Toxicity Index			
Process unit	refrigeration installation		
Working fluid in process unit	ammonia	Material factor	4
State of operation	process storage		
GENERAL PROCESS HAZARDS			penalty
base factor			1.00
• enclosed or indoor process unit::			/
• access			/
• drainage and spill control			0.50
General process hazards (F1)			1.50
SPECIAL PROCESS HAZARDS			
base factor			1.00
• toxic materials			0.60
• sub-atmospheric pressure			/
• operation in or near flammable range			/
• relief pressure			0.39
• low temperature			/
• quantity of flammable and unstable materials			0.64
• corrosion and erosion			/
• leakage - joints and packing			/
• use of fired heaters			0.10
• rotating equipment:			/
Special process hazards (F2)			2.73
Unit hazard factor (F3 = F1 x F2)			4.10
Fire & Explosion index (F&EI = F3 x MF)			16

8.1.4 Conclusion

As illustrated above, calculation of the F&EI is relatively simple, requiring only basic information regarding the installation and the process involved. As shown for the process storage of ethylene, the F&EI also provides a tool for the evaluation of specific installation conditions that are significant in relation to accidents. From the area of exposure calculation, a number of conclusions can be drawn.

- For the process storage of liquefied gases the F&EI is valid for each vessel. However, if more vessels are installed in line, adjacent to each other, each will fall within the area of exposure of neighbouring vessels. This implies that domino effects have to be taken into account and, in addition, that measures taken to improve safety must be applied to all the vessels (all being considered as a single installation unit).
- The domino effects on other installations have also to be taken into account. Installations for fire-fighting purposes, e.g. the fire pumps or the fire water supply within the exposure area, may also be damaged as the result of an accident, leading to an escalation of the latter's effects. Other vital installations such as control rooms should also be kept outside the exposure areas.

It is evident that, with a limited amount of knowledge about the installation and using a relatively rapid evaluation procedure (F&EI), it is possible to classify installations in respect of their fire and explosion hazard. In addition, by drawing the exposure areas on a ground plan, this technique can be used to support decisions regarding the location of new installations.

8.2 Assessing the Toxic Hazards

The Toxicity Index can easily be calculated for the industrial installations described above. As for the F&E Index, minimum amounts of working fluids are assumed to be in each process unit.

For the process storage of ammonia the hazard factors F_1 and F_2 are 1.50 and 2.73, respectively (Figure 8.3). Using the formula given in Figure 8.3 and the toxicity factor for ammonia of 3.25, the Toxicity Index is 20.25. Equivalent calculations for the process storage of ethylene and for the ethylene compressor give values of 7.86 and 6.16, respectively.

These results indicate that the range for the Toxicity Index is narrower than that for the F&EI. This reflects the narrow range associated with the toxicity factor (from 0 to 4.5). Furthermore, most non-toxic flammables have a toxicity factor of 1. It is also clear from the hazard factor calculations in Chapter 7 that toxic working fluids that are also flammable will be much more heavily penalised than others. Most of those listed in Table 7.10 fall into this category, R40, R160 and R1130 having a material factor of 21 or 24.

9. TECHNIQUES FOR EVALUATING SPECIFIC EFFECTS

This chapter examines a number of specific models which are used to estimate the effects of accidents involving heat pumps and refrigeration equipment. The purpose is to highlight the most important aspects and to given an insight into the calculation assumptions made.

These models are then applied in Chapters 10-13 for typical installations and different working fluids. To analyse the effects of an accident in a quantitative way one has to be aware of the different stages that can be involved. A number of distinctions are therefore made between:

- **Emission and evaporation**
  Calculation of the total amount of working fluid released and its distribution between the different phases.
- **Dispersion of gases**
  Calculation of the concentration of gases in the surroundings after an emission of working fluid has occurred.
- **Effects**
  Calculation of the effects including pressure waves, heat radiation, concentration of toxic gases.
- **Vulnerability**
  Determining, from the effects, the impact on persons.

Physical models are used to derive a calculation procedure for each of these stages. Annex 3 gives a general description of the assumptions, the input required, the output obtained, the validity range etc for each model. The assumptions and validity limits are particularly important and should be carefully studied.

Because the calculation requires data on the properties of the various working fluids, a database has been set up to provide the necessary information. Other fluids can be added by the user.

9.1 Emission and Evaporation

9.1.1 Emission

Determining the amount of a hazardous product released is fundamental to calculating the subsequent effects of that release. A basic distinction is made between:

- an instantaneous release;
- a continuous release.

In practice, the difference between the two types of release may not always be clear.

Instantaneous release

The best example of an instantaneous release is the sudden breakdown of a vessel which results in the release of its contents. Scenarios where the total release occurs in only a short time can also be regarded as instantaneous releases. The amount of product released in such cases must be estimated directly from the layout of the installation, the circumstances of the accident etc.

Continuous release

Where continuous release is involved, a distinction is made between:

- a gas jet release;
- a two-phase jet release;
- a liquid release.

In each case a constant release rate is assumed.

Gas jet release

The (constant) emission rate for a gas jet release of working fluid from a pressurised vessel can be calculated using a generally accepted formula. Depending on the pressure in the vessel, a distinction is made between critical and sub-critical flow.

The release rate from an opening in a vessel wall is also valid for the release through a pipe as long as frictional effects can be ignored (i.e. the pipe is short). The release rate determined in this way will be a conservative estimate if frictional effects become important.

Two-phase jet release

If a vessel is filled with a liquefied gas under pressure and a pipe connected to the liquid ruptures, a two-phase flow will occur if the temperature of the liquefied gas is higher than its atmospheric boiling point. The initial evaporation that takes place is called flashing.

It is very important to note that this two-phase flow is only possible if it can develop in the pipe. The minimum pipe length required to achieve a two-phase release will depend on the specific circumstances but, as a rule of thumb, a length of at least 10 cm is necessary. A puncture in the vessel wall below the liquid level will result in a liquid release giving rise to evaporation (flashing) outside the vessel. In this case higher release rates are to be expected.

Models are available which estimate the release rate for a two-phase flow from the conditions of the fluid in the vessel prior to release. A generalised homogeneous equilibrium flow correlation model is used [56]. However, the results are very sensitive to the input relating to the properties of the working fluid. The calculation will therefore only be valid for a release in which the condition at the inlet of the opening corresponds to the one for which the properties are given in the database (20°C, saturation pressure). If other conditions obtain, the results will provide only a rough estimate.

Liquid release

The release of a liquid under pressure can be calculated using a generally accepted formula.

9.1.2 Evaporation

A number of distinctions can be made with regard to evaporation[1].

- When a pressurised liquefied gas is released, the fraction that evaporates immediately can be found from the heat of evaporation, the specific heat of the liquid and the difference between the temperature of the released fluid and its atmospheric boiling point.
- The evaporation from liquid pools is mainly determined, initially, by the heat conduction from the soil to the liquid. Freezing of the soil will, however, reduce the conduction of heat and, after a certain time, any evaporation will be due mainly to mass transfer by diffusion to the ambient air.

  The calculation procedure is limited to the evaporation of boiling liquids on a non-penetrating soil. A distinction is made between average soil with an 8% water content, dry sand and gravel. The rate of evaporation is a function of time ($\sim t^{1/2}$) and decreases rather quickly.

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[1] The evaporation of liquid pools on water is not considered

- The evaporation of non-boiling liquids is determined by mass transfer. The evaporation rate is strongly dependent on the air speed above the liquid pool surface. Calculations will therefore only be valid if the wind speed is not equal to zero (> 1 m/s). The results obtained are the maximum values that can initially be expected and can be regarded as conservative estimates.

9.2 Dispersion of Gases

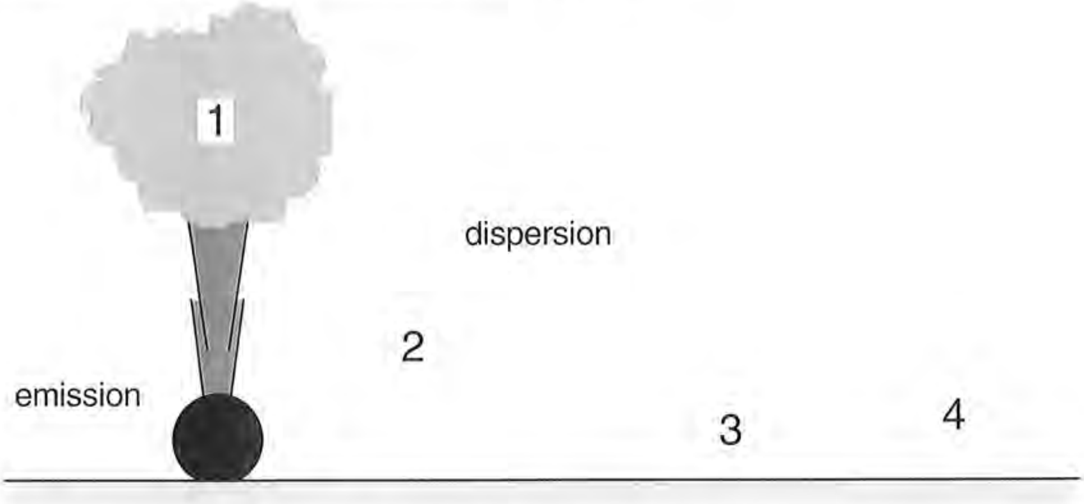
The degree of dispersion of the gases released depends on the density of the gases in relation to air, with a distinction being made between light gases, neutral gases and heavy gases.

The density of the dispersed gases is important in relation to the buoyancy forces. The models for neutral and heavy gases therefore differ substantially.

Less attention is given in modelling to the dispersion of light gases because only a small proportion of the substances under discussion fall into this category. In addition, the possible effects will be less severe because of the rising motion of these gases. Modified neutral gas models can take into account the effect of the lower density of light gases. Furthermore, in the calculations, neutral gas models can be used to give a conservative estimate.

The major steps involved in modelling the continuous release of a heavy gas are shown in Figure 9.1.

Figure 9.1 Major steps in modelling a hazard gas release



For the dispersion calculation the type of release is also defined:
- continuous release;
- instantaneous release.

As already noted for the emission of a fluid (Section 9.1.1) the difference between the two types of release will not always be clear. In a scenario where the type of release is in doubt, calculation for both types is advised. The worst case can then be considered. It will, however, become clear that the worst situation also depends on the distance from the point of release. The distance of interest must therefore be determined first in order to decide which dispersion situation is the worst.

Dispersion also depends on external circumstances such as the stability of the atmosphere, wind speed, the local site layout (terrain, houses, buildings) etc. The detailed modelling of these external constraints is beyond the scope of this work.
For this report a more simplified calculation scheme has been implemented. The gas concentrations found in the environment are calculated for a worst and a mean dispersion situation where a flat and open terrain is assumed. The same calculation scheme is followed for the neutral as well as the heavy gases and for continuous as well as instantaneous releases.

Because many installations are located inside a building, a model has also been developed for estimating the 'inside' concentration where a release occurs under these conditions.

9.2.1 Dispersion of a neutral gas: continuous release

The dispersion of neutral gases is generally calculated following the so-called Gaussian dispersion relationship. This means that a Gaussian distribution of the concentration in the downwind direction, perpendicular to the wind direction and in the vertical direction is assumed. The general formula, assuming a point source, is [57]:

$$C(x,y,z)=\frac{m}{2\pi\, u_w\, \sigma_y(x)\sigma_z(x)}\ \exp\left(-\frac{y^2}{2\sigma_y^2(x)}\right)\left[\exp\left(-\frac{(z-h)^2}{2\sigma_z^2(x)}\right)+\exp\left(-\frac{(z+h)^2}{2\sigma_z^2(x)}\right)\right] \tag{9.1}$$

where:

C = the concentration at the specified point with co-ordinates (x, y, z) (m)
m = mass release rate (kg/s)
u_w = wind speed (m/s)
h = height of the point source (m)
σ_y, σ_z = spreading parameters (m)

This model allows calculation of the downwind concentrations when the cloud becomes stationary, i.e. when the release rate equals the dilution rate. The formation of this stationary cloud implies a minimum time of release. It is possible to check quickly if a cloud can be formed within a certain time using the following rule of thumb:

> *the wind speed multiplied by the time since release gives an estimate of the maximum distance where concentrations of the working fluid can be expected.*

Differences between Gaussian models relate to the parameters used to describe the spreading of the gases in the atmosphere (expressed by σ_y and σ_z in the formula above).

9.2.2 Dispersion of a neutral gas: instantaneous release

The models for the dispersion of neutral gases after an instantaneous release are comparable to those for the continuous release [57]. In this case too the models are based on a Gaussian dispersion in the atmosphere where parameters used to determine the spreading of the cloud can differ from one model to another.

In the model used, the downwind concentration is calculated at a certain place and at a certain time after release.

9.2.3 Dispersion of a heavy gas: continuous release

Many models are available for calculating the dispersion of heavy gases. Most are too complex for the purposes of this report. One has therefore been chosen that has its origins in dimensional analysis [58]. A relationship between the different dimensional groups has been determined on the basis of experiments (to scale).
It is clear from Figure 9.1 that the more diluted the heavy gas becomes, the more the effect of buoyancy will decrease. The model is applied at the stage where atmospheric turbulence is the main determinant of further dispersion. For concentrations of more than 1 vol % a heavy gas dispersion is assumed. For lower concentrations (e.g. for toxic gases) the neutral gas dispersion model is used.

9.2.4 Dispersion of a heavy gas: instantaneous release

The same approach is used as for the continuous release of heavy gases. The maximum concentrations over the time at the given distance are calculated [58].

9.2.5 Concentration inside a room (or apparatus)

The concentration within a room (or apparatus) where gases have been released within that room or apparatus has also been modelled. This model assumes a homogeneous concentration within the room, with no enclosure of gas at specific locations. This assumption implies the absence of any distinction between light, neutral and heavy gases. The calculation can be made for both continuous and instantaneous releases, taking into account a given ventilation rate and room volume.

The remaining oxygen concentration within the room is calculated at the same time in order to determine whether asphyxiation has to be taken into account.

9.3 Effects

The effects that can be expected in the case of an accident will depend in the first place on the properties of the working fluid involved but also on the specific scenario of the accident. The effects examined below will therefore be valid for an assumed scenario and working fluid[1].

The most important effects of an accident are:
- overpressure;
- fragments;
- heat radiation;
- toxic concentration;
- absence of oxygen.

Freezing is also to be expected when contact with very cold liquids occurs. Calculations are not necessary in this case.

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[1] It is clear that ignition of a cloud is only relevant if in the first place a cloud is formed and, additionally, the cloud contains a flammable gas

9.3.1 Overpressure

Overpressure can result from:

- a mechanical explosion:
  - rupture of a vessel filled with a liquefied gas under pressure (BLEVE);
  - rupture of a vessel filled with a gas under pressure;
- a chemical explosion:
  - explosion of an unconfined flammable cloud (UVCE);
  - internal (confined) explosion.

Mechanical explosion: BLEVE

A BLEVE or boiling liquid expanding vapour explosion occurs when a vessel containing a liquefied gas under pressure suddenly breaks down completely. The liquid phase will evaporate explosively as a result of the pressure drop. This evaporation may cause damage to the surrounding environment as a result of the pressure wave and/or the fragments generated.

The expansion energy that is released upon rupture of the vessel that contains a liquefied gas under pressure consists of two components:

- the energy released as a result of the expansion of the gas phase: this is determined by the volume of the gas phase and the pressure before breakdown;
- the energy released as a result of the explosive evaporation of the liquid phase: this is determined by the liquefied mass and the degree of overheating before breakdown (overheating = the difference between the temperature of the liquefied gas before release and its atmospheric boiling point).

The expansion energy will be distributed mainly between the kinetic energy of the fragments and the compression work in the blast wave. Only a minor (negligible) part is used for the deformation and breaking of the reservoir. The typical distribution of the expansion energy is given in Table 9.1 [59].

Table 9.1 Distribution of the expansion energy E_e

Type of rupture	Energy in pressure wave	Energy in fragments
Ductile	$0.4\ E_e$	$0.6\ E_e$
Brittle	$0.8\ E_e$	$0.2\ E_e$

To determine the expansion energy an isentropic expansion (i.e. without heat exchange) can be assumed. This is a conservative assumption.

A brittle rupture is only expected at very low temperatures. This suggests that the expansion energy is much lower than for the rupture of a vessel at normal or higher temperatures. The energy in the pressure wave will therefore be higher for a ductile rupture than for a brittle one, even if one takes into account the greater part of the energy found in the pressure wave for the brittle rupture (Table 9.1). From the calculated expansion enegy (E_e) and the type of rupture, the maximum overpressure in the pressure wave can be estimated using the following equation:

$$\Delta p = \frac{3.172}{(r/E_e^{1/3})^{4/3}}\ p \qquad (9.2)$$

where:

E_e = expansion energy in the pressure wave (kg TNT equivalent[1])
r = distance from the failing vessel (m)
p = pressure in the environment (bar)
Δp = overpressure (bar)

The scenario that results in a BLEVE can be the overfilling of a vessel or the exposure of the vessel to an external fire. If the total heat capacity of the liquid phase is high enough (a large vessel filled mainly with a liquid phase) the contents will be heated only slowly in the case of an external fire. The rupture will then be caused by the weakening of the vessel as a result of the high wall temperatures. The increase in the temperature of the liquid will, in such a case, be rather limited - an important factor when determining the expansion energy.

Mechanical explosion: vessel with gas under pressure

If a vessel filled with gas under pressure suddenly fails, a pressure wave and/or fragments can be expected. In this instance only the expansion of the gas phase has to be taken into account. As for a BLEVE an isentropic expansion is assumed, and the same distribution of this expansion energy is taken as in Table 9.1. For a ductile rupture the overpressure is estimated using Formula 9.2, taking into account an efficiency of blast wave compression by the energy released of 0.4.

Chemical explosions: UVCE

The chemical explosions considered here are reactions of the combustion type. An unconfined vapour cloud explosion (UVCE) can be generated if an unconfined cloud of a flammable vapour is ignited. The scenario of a UVCE first assumes the release of a flammable working fluid vapour. The dispersion of the gas then results in the formation of a flammable cloud that can be ignited.

The amount of flammable gas in the explosive range (between the LEL and UEL) is an important parameter that largely determines the probability of ignition and the probability that this ignition results in an explosion. To estimate the effects of the pressure wave that results from such an explosion, the theoretical explosion strength is estimated as:

$$W_t = M \times S \qquad (9.3)$$

where:

M = kg of vapour in the cloud at concentrations between the explosive limits
S = heat of combustion of the vapour

In reality, part of the total heat released is used to produce work (to generate a pressure wave). The real explosive strength is thus a fraction of the theoretical one and can be expressed as:

$$W_r = \eta \times W_t \qquad (9.4)$$

where:

η = efficiency of the explosion

---

[1] 1 kg TNT = 4.18 MJ

The efficiency of the explosion is a function of the amount of vapour in the cloud at concentrations between the explosive limits (also called the explosive mass). A conservative estimate of the efficiency is 0.10. The overpressure can be calculated using Formula 9.2 and substituting the real explosive strength for E. If the cloud explodes near the ground the reflection of the pressure wave has to be taken into account. As a rule of thumb this can be done by doubling the real explosive strength. In the computer model developed here the calculation model used to determine the overpressure includes an estimate of the efficiency as a function of the explosive mass.
The ignition of an unconfined flammable cloud does not necessarily result in an explosion. Experience shows that the explosive mass in the cloud should be at least one ton to give rise to the build-up of overpressure in the environment with a relevant probability of explosion (about 1%). A UVCE can only be expected for large releases (industrial installations). If the ignition does not result in an explosion, a flash fire occurs (see Section 4.3.3).

Where the release is instantaneous a semi-spherical cloud will initially be formed as a result of the expansion of the fluid. As already noted for a BLEVE, an initial flashing will occur. At the same time the liquid phase is broken up into small drops and mixed with the ambient air. This results in the evaporation of most of the liquid in a short time. For the calculations it is assumed that all the instantaneously released fluid will initially be found in the cloud.

Where the release is continuous the dimensions of the cloud will generally be much smaller and so will the explosive mass.

Chemical explosion: internal explosion
Unconfined vapour cloud explosions are only to be expected for large releases. When considering smaller installations and/or releases, a realistic scenario is that of a room filled with a flammable mixture which is ignited. For the explosion of a flammable working fluid at stoichiometric concentration in a confined space, the maximum pressure that can be expected is about 6-10 bar if the room remains intact. For hydrocarbons the pressure rise is about eight times the initial pressure for a concentration approaching stoichiometric. Richer or leaner concentrations will reduce the explosion pressures considerably.

The pressure rise in the confined space can be estimated using the following equation:

$$\frac{dp}{dt} = \frac{k}{V^{1/3}} \qquad (9.5)$$

where:
p = pressure (bar)
t = time (sec)
V = volume of the confined space (m^3)
K = gas constant (bar m/sec)
Typical values for K (gas constant) are 100 bar m/sec.

A room in which an internal explosion occurs will not withstand the expected overpressure and considerable damage can therefore be expected.

9.3.2 Fragments

If an explosion occurs in a closed system, fragments may be turned into missiles which may cause effects in the surrounding environment as a result of impact. In addition, other objects in the vicinity may be turned into missiles by the pressure wave of an explosion.

In the case of large vessels containing liquefied gases fragments may be projected up to 1000 m from the vessels.

9.3.3 Fire

The different types of fire that can be identified are:

- jet flame;
- fire-ball;
- flash fire;
- pool fire.

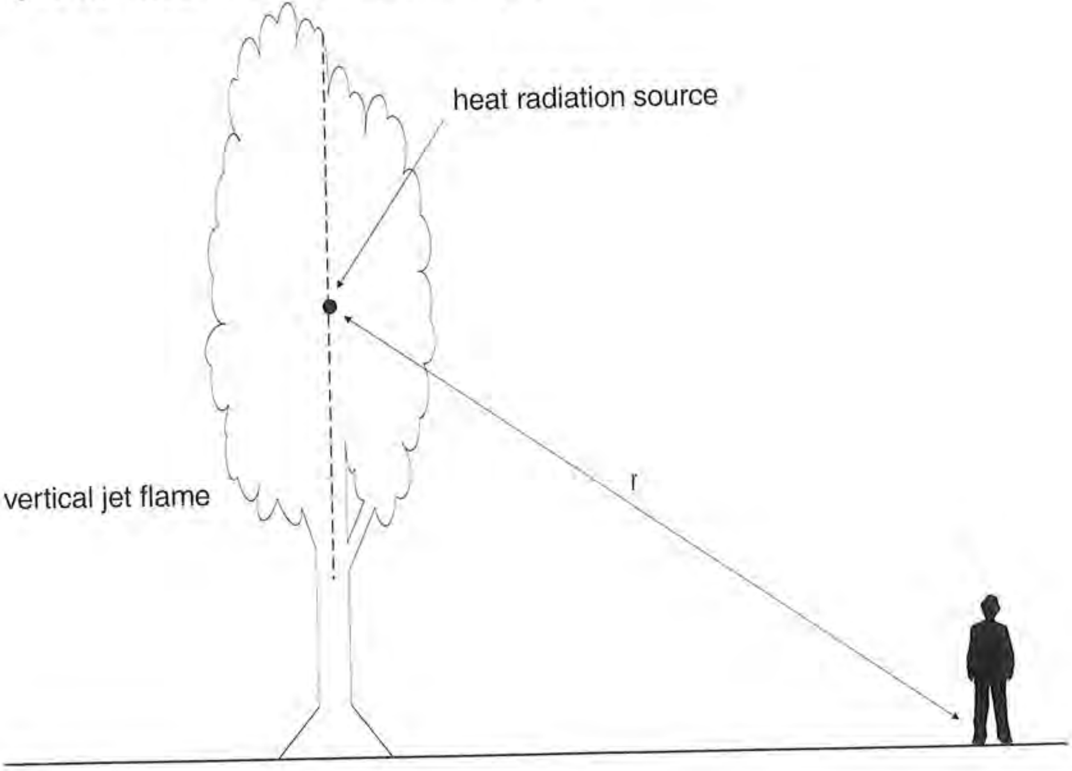
Different models are used to estimate the emitted and incident radiation heat.

Jet flame

A jet flame is a flame originating in an orifice. Ignition of a flammable gas release with a sufficient velocity results in the formation of diffusion flames in which a pure gas leaves the orifice and the air of combustion has to diffuse to it from the surrounding atmosphere. In such a case the flame length is independent of the velocity of the working fluid and the flame temperature is the highest of the various types of fire. The model used is also valid for turbulent diffusion flames.

The heat radiation is calculated by modelling the flame using a point source located at the centre of the flame (Figure 9.2).

Figure 9.2 Heat radiation from a vertical jet flame



The incident heat flux can be found using the following equation [60]:

$$q = \frac{FQ}{4pr^2} \qquad (9.6)$$

where:

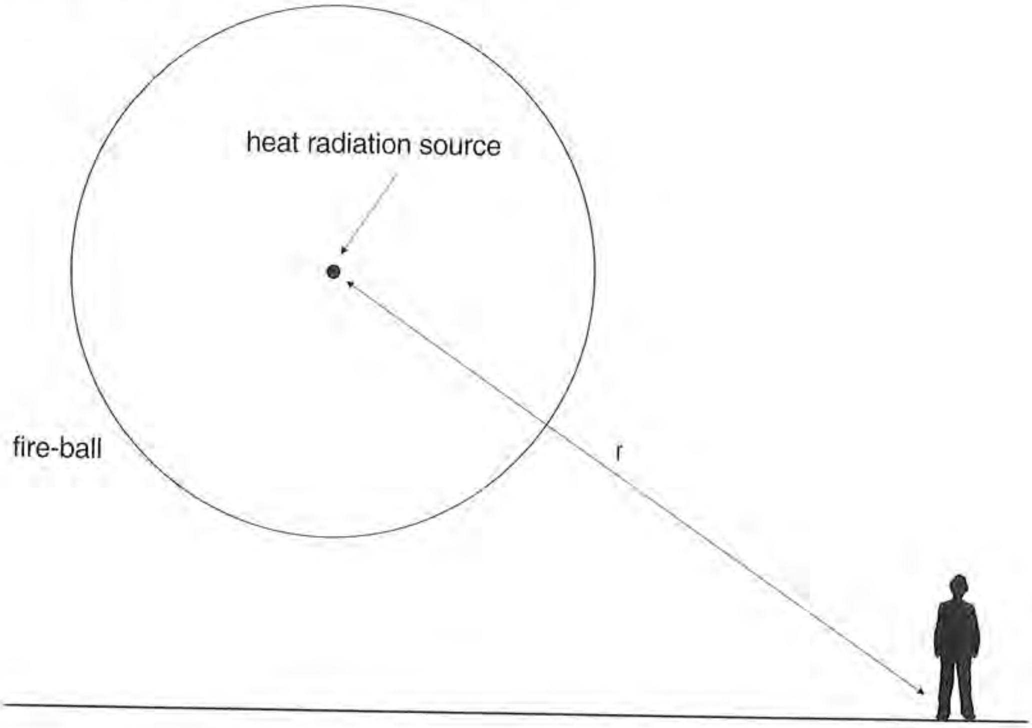
q = incident heat flux (W/m^2)
Q = energy release rate from combustion (W/s)
r = distance from flame centre (m)
F = fraction of combustion energy resulting in radiation

The use of the fraction (F) of combustion energy resulting in thermal radiation signifies that details of the combustion process, the combustion efficiency etc are not taken into account because quantitative information regarding these complex processes is not available. This fraction is deduced from experiments and can be found in the literature. For hydrocarbons it lies between 0.2 and 0.4.

Fire-ball

As already noted, a BLEVE occurs when a vessel containing a liquefied gas under pressure suddenly breaks down completely and, as a result, the liquid phase evaporates explosively. If the released fluid is flammable and is ignited when the release occurs, a fire-ball results. This means that, in addition to the effects of overpressure and fragmentation, the effects of heat radiation also have to be expected. Figure 9.3 shows a schematic of a fire-ball. The radiation is calculated assuming a point source at the centre of the fire-ball and an emittance fraction (as for the jet flame).

Figure 9.3 Heat radiation from a fire-ball



Models exist for estimating, as a function of the released mass, both the diameter of the fire-ball and its duration [61]. Generally the duration will be limited (some tens of seconds). Where small amounts of working fluid give rise to a fire-ball, the effects of direct flame impact are more relevant as exposure times are limited.

Flash fire
The ignition of an unconfined flammable cloud results in a flash fire if no build-up of pressure occurs. The main effect will result from the combustion of the flammable mixture.

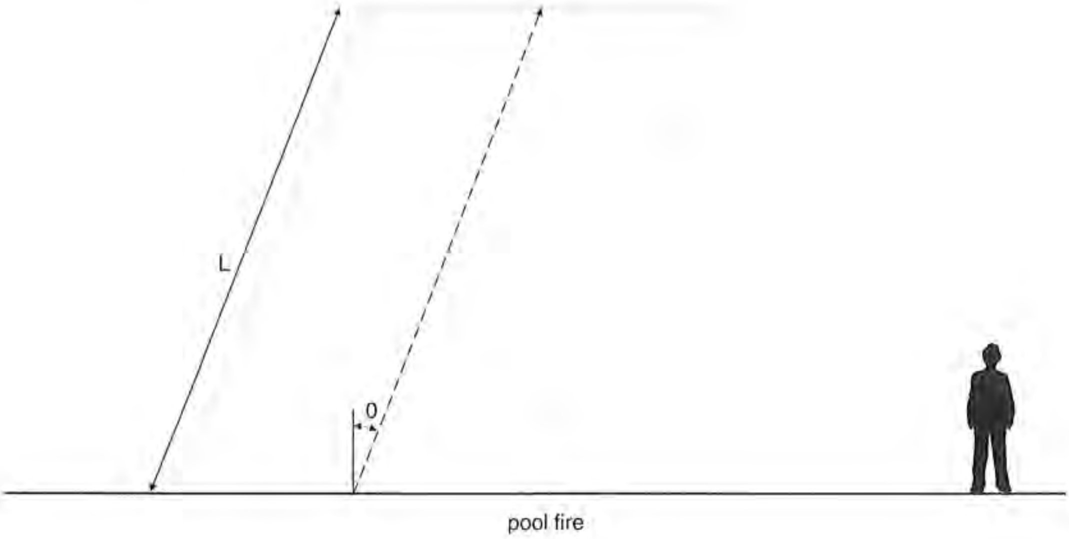
Models for this phenomenon are not well developed. From observations, however, it can be accepted that serious effects (severe injury or death) are to be expected within the flammable cloud, i.e. where the concentration is above the LEL [62]. These effects will result mainly from burning from direct flame contact and the ignition of clothing, and from lack of oxygen.

Pool fire
A liquid release resulting in the formation of a pool might result in a pool fire if ignition of the flammable fluid occurs. The heat radiation intensity in the surrounding environment can be established from the size and shape of the fire and the emitted heat at the surface of the flames.

A distinction can be made between a confined and an unconfined pool. In the case of the latter, the degree of spread will be determined by local circumstances such as the slope and roughness of the surface. Where the release is continuous, an unconfined pool will spread out until the total burning rate equals the release rate (assuming that the total release period is long enough).

As shown in Figure 9.4, the base of the flames is formed by the liquid pool. In the case of a circular pool the shape of the fire resembles a cylinder that may be tilted under the influence of a cross-wind. Non-circular pools may be converted to their circular equivalent by calculating the diameter so that the area remains the same.

Figure 9.4 Heat radiation from a pool fire



Basic to the calculations is an estimate of the liquid burning rate. Models are available for calculating the dimensions of the flames, assuming a circular pool. Apart from the flame length (L), the tilt angle (θ) is also determined. It should also be noted that the base of the flames will extend in the downwind direction under the influence of that wind. This effect is also taken into account.
The incident heat flux is calculated using the following formula:

$$q = E_{surface} V_f \tag{9.7}$$

where:

q = incident heat flux (W/m^2)
$E_{surface}$ = mean heat radiation intensity at the surface of the flames (W/m^2)
V_f = view factor

The heat flux emitted at the surface of the flames is estimated on the basis of a correlation that is valid for hydrocarbons [63]. The view factor takes into account the area and orientation of the flames in order to determine the amount that is emitted in the direction of the receiver. With respect to the orientation of the surface where the incident heat radiation is calculated, a conservative orientation is assumed (maximum heat radiation). The partial absorption of the radiated heat by water and carbon dioxide in the ambient air is not taken into account in this report.

The duration of a pool fire will be determined by the total released mass, the burning rate and the size of the pool.

9.3.4 Toxic concentration

This report assumes exposure to toxic vapours only. This implies that the released toxic fluid must be a vapour or an evaporating liquid. The expected concentrations in the surrounding environment are estimated using the dispersion models mentioned above (Section 9.2). A procedure is also available for calculating the concentration resulting from the release of a toxic fluid in a room.

9.3.5 Absence of oxygen

The absence of oxygen is only relevant if the gases are not toxic (i.e. if toxic effects are of secondary importance). The exposure time is relevant as well as the concentration.

Effects resulting from a reduction in the amount of oxygen in the atmosphere tend to occur when the oxygen level is below some 15 vol %. In such a case the concentration of the working fluid vapours must be at least 30%. It must be clear, however, that these high vapour concentrations will only be possible in confined spaces with little or no ventilation. Therefore, apart from the calculation of inside vapour concentrations, the remaining oxygen concentration is also given in the computer program. Where release occurs in the open air, an absence of oxygen will only be possible very close to the release opening (in the case of continuous release) or, in the case of a large, instantaneous release, where high concentrations of the released fluid can be expected.

Asphyxiation has only to be considered if the working fluid itself has no relevant toxic effects (i.e. the inhalation of concentrations of < 20-30% has no adverse toxic effect on people). This distinction will, in most cases, depend on the period of exposure. Exposure to high concentrations (20-30 vol %) for longer periods (more than one hour) may result in health effects even in the case of the so-called non-toxic working fluids. For accidental releases the exposure times will normally be shorter with the result that, on the short time scale, asphyxiation becomes relevant for non-toxic working fluids.

9.4 Vulnerability

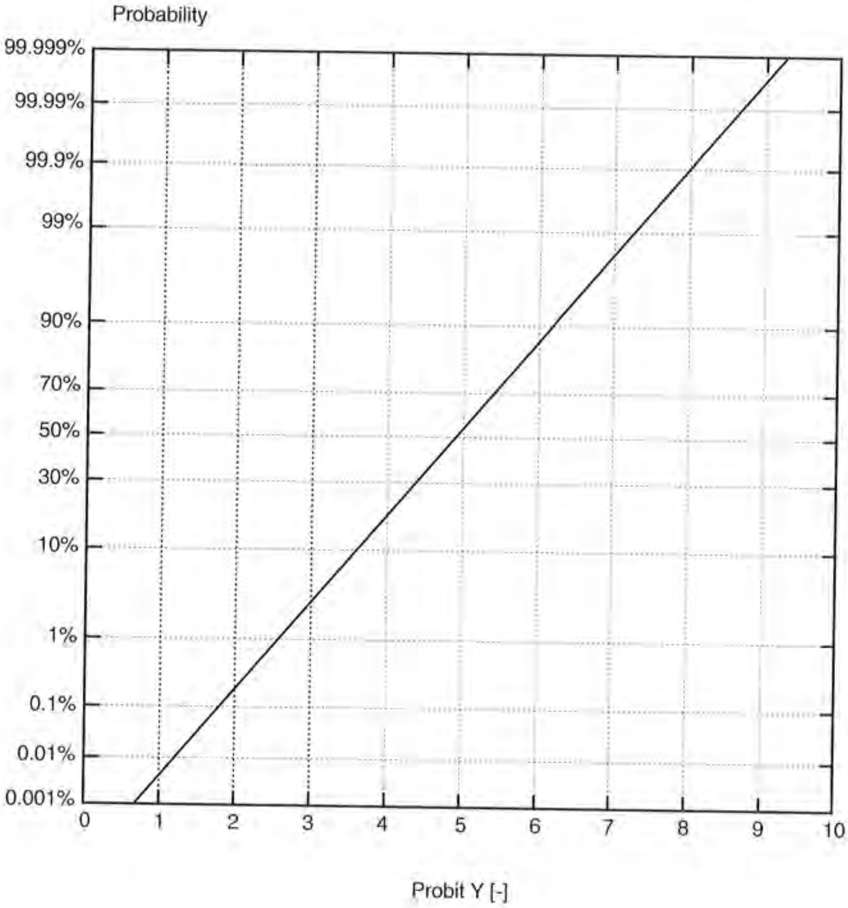
The purpose of the vulnerability models is to determine the relationship between the intensity of the effects (overpressure, heat radiation etc) and the degree of injury which can result from them.

No quantitative models are available for the effects of freezing and asphyxiation. However, freeze burns are only to be expected close to the installation. The effects of asphyxiation have already been described qualitatively. For a quantitative estimate of the impact of the effects of overpressure, heat radiation and toxic concentrations, use is made of probit functions [64, 59]. It has been found that the relationship between effects and the probability of injury tends to follow a log normal distribution.
The probit Y (probability unit) is a random variable with a mean value of 5 and a variance equal to 1. It is related to the probability (P) by the following equation:

$$P = \frac{1}{\sqrt{2p}} \int_{-\infty}^{y-5} \exp\left(-\frac{u^2}{2}\right) du \qquad (9.8)$$

The probability that ranges from 0 to 1 is generally replaced by a percentage (0-100%). The relationship between the probit and the probability is given in Figure 9.5.

Figure 9.5 Relationship between probit and probability



The general form of the probit function is:

$$Y = a+b \ln V \tag{9.9}$$

The probit Y is a measure of the percentage of vulnerable items which sustain injury or damage. V is a measure of the effect which harms the vulnerable resource and expresses the intensity of the effect. The constants a and b can be calculated from the data expressing the relationship between the intensity of the effect and the degree of injury.

It is, however, emphasised that the probit equations are very tentative and approximate. This means that the proposed probit functions must be used with great care. Probit functions are given for the following effects:
- overpressure;
- heat radiation;
- toxic concentration.

9.4.1 Overpressure

With respect to the effects of overpressure on people, a distinction can be made between:
- primary effects;
- secondary effects.

Primary effects result from the direct impact of a pressure wave on people. A possible scenario is where someone standing in an open field is killed or wounded as a result of the impact of a pressure wave. Experience indicates that the overpressure must be > 1 bar in this case.

Secondary effects are those indirectly caused by the pressure wave. An example of this scenario is when a pressure wave causes the demolition of a window pane allowing the glass fragments to be turned into missiles. The effects resulting from the impact of these fragments are called secondary effects. Injury to people behind a window pane from the impact of glass missiles is possible if the blast wave overpressure is greater than 40 mbar. However, this implies that the impact of the pressure wave is perpendicular to the window pane and that this pane is made of a single glass layer.

Secondary effects can also result from falling bricks, tiles or other building fragments. In this case the overpressure must be more than 100 mbar. Table 9.2 gives an overview of the type of damage that can be expected as a function of the peak overpressure.

Limit values, based on the figures for peak overpressure shown in Table 9.2, are given in Table 9.3. The calculation program is provided with a probit function (i.e. the constants a and b) to determine the probability of death or severe injury as the result of a pressure wave. The probit functions available for calculating the effects require only the input of the overpressure (i.e. the variable V given above). However, this function incorporates the primary as well as the secondary effects and is thus an estimate of the probability in the worst situation. Figure 9.6 demonstrates the probability of death or severe injury as determined by this probit function.

Figure 9.6 Vulnerability to overpressure

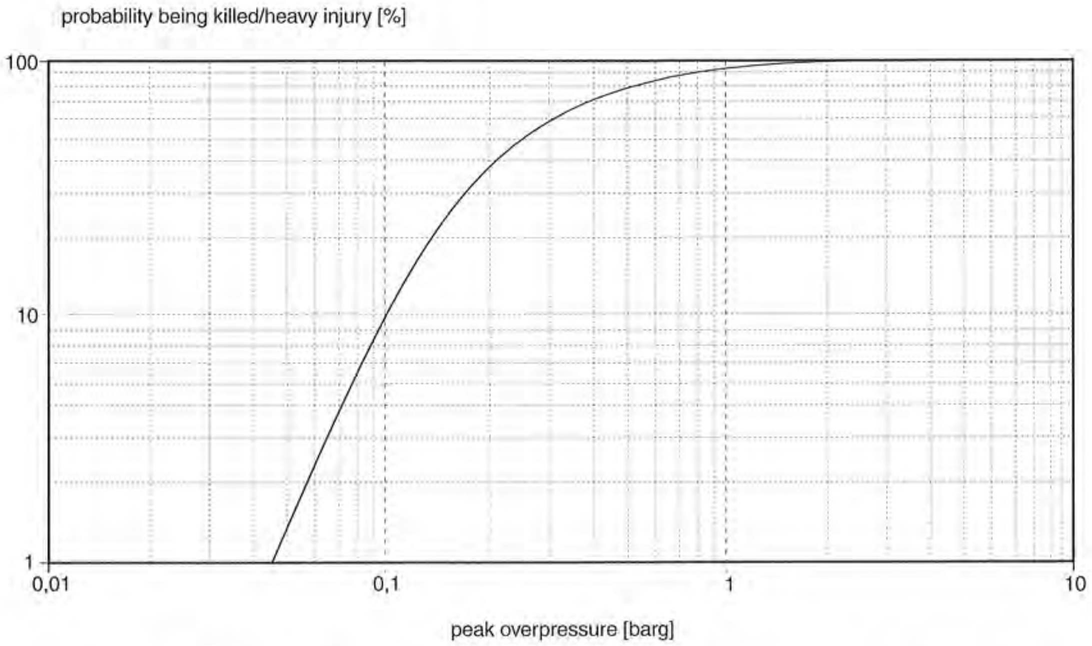


Figure 9.6 should, however, be used with caution. If the overpressure is limited to only some tenths of one bar, the probability of injury is associated mainly with the formation of secondary fragments (the chance of being killed when exposed to an overpressure of 0.1 barg is almost nil when standing in the open field). Beyond ± 0.1 barg the total or partial collapse of houses caused by overpressures (and the associated fragmentation) assumes a greater significance. However, only at high overpressures (> 1 barg) is death likely from the impact of a pressure wave.

Table 9.2 Expected type of damage as a function of the peak overpressure

dP (barg)	Type of damage	Ref
0.01	Breaking of window-pane, injuries caused by falling glass possible	[57, 65]
0.02	Temporary deafness	[57]
	Safe distance: no major damage with a probability of 99%	[65]
0.03	Killing caused by fragments of broken glass possible	[57]
0.04	Secondary injuries from fragments of broken glass negligible	[66]
0.05	Damage to roofs of houses	[57]
0.07	Partial damage to houses	[65]
0.10	Damage to brick walls	[57]
0.14	Walls fall apart partially	[65]
0.14	Rupture of ear-drum	[67]
0.30	Rupture of ear-drum	[57]
	Complete destruction of houses	[65]
1.0	Lung damage	[57]
	Probability of being killed as a result of lung damage is about 1%	[67]
2.0	Direct killing pressure wave	[57]

Table 9.3 Limit values for peak overpressure

Peak overpressure (barg)	Type of damage
0.02	Safe distance, only glass breaking
0.04	Injuries by fragments of glass
0.06	Minor damage to houses
0.10	Major damage to houses

Probit functions are also provided for estimating the probability for ear-drum rupture and lung haemorrhage (both primary effects). The purpose is to show that primary effects are mainly to be expected at higher overpressures.

9.4.2 Heat radiation

Determining the effects of heat radiation on people requires details of the exposed heat radiation level (I) and the exposure time (t). A combination of both in the form of $t \times I^{4/3}$ forms the variable V in the probit function.

The probit functions available make it possible to estimate the chance of death from exposure to heat radiation and also the chance of first and second degree burns.

Expected damage as a function of the heat radiation intensity is given in Table 9.4.

Table 9.4 Exposure limits for damage from the heat radiation of pool fires

Limit (kW/m^2)	Expected damage
1.5	Pain limit
4.5	First degree burns
5.0	Glass damage
12.5	Ignition of wood if ignition source available
> 10.0	Damage to installations (10 kW/m^2 is the limit for electrical cables)
25.0	Ignition of wood when exposed for a long period

Table 9.5 gives the maximum allowable exposure limits for evaluating pool fires.

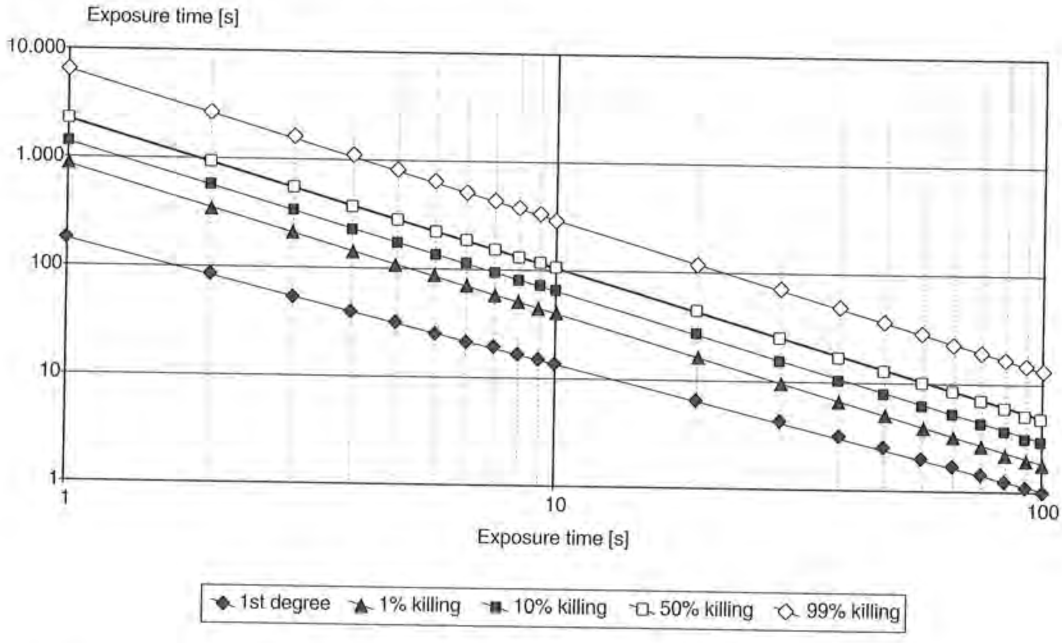
Table 9.5 Maximum allowed exposure to heat radiation

Limit (kW/m^2)	Maximum allowed exposure
1.0	People, exposure for long periods
3.0	People, escaping from radiation
10.0	People, exposure for 5 seconds
10.0	Installations, also storage tanks

The effects of heat radiation can be estimated from the probit function. In Figure 9.7 the vulnerability is expressed as a function of the incident heat radiation and the exposure time.

It is assumed that flame contact (being inside a fire-ball, jet flame or burning cloud) will always result in death. Injury by exposure to heat radiation is assumed to occur from second degree burning (for an exposure time of 30 seconds this means a heat radiation ≥ 7 kW/m^2).

Figure 9.7 Vulnerability to heat radiation



9.4.3 Toxic concentration

Assessment of the effects of exposure to toxic gases (by inhalation) requires details of the concentration (C) of the toxic gas and the exposure time (t). For a mortality-based probit approach both factors are used to derive the variable V from the probit function. The combination of the factors takes the form of C^n x t which, from experimental observations, is found to be a general relationship that may hold for acute lethality. This combination can be called the 'toxic load'[1]. The constants n, a and b are functions of the toxic gas involved and are extracted from experimental data. In this report only the direct effects on human health arising from the release of a toxic substance in the atmosphere are considered.

The database provided with the calculation program only gives the probit constants for those toxic gases where a probit function is found in the literature. For the vast majority of hazardous substances the most readily available information on the toxic effects of the airborne substance is the atmospheric concentration and the exposure time resulting in death in laboratory animals (which give rise to the LC_{50} values).

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[1] This is not equivalent to the administered 'dose' which is expressed as concentration x time in inhalation toxicology

For products added to the database or for those where LC_{50} values are available, a calculation scheme is provided to determine the constants of the probit function from the LC_{50} values [64]. The scheme is based on conservative assumptions as to how the results of toxic effects on animals apply to people. These assumptions include the values 2 and 1 for the parameters n and b respectively. They also include a safety factor. This takes into account, for example, the heterogeneity of the population. It has been estimated that the proportion of the human population that should be considered to be particularly vulnerable to the health effects of toxic gases constitutes about 25% of the general population.

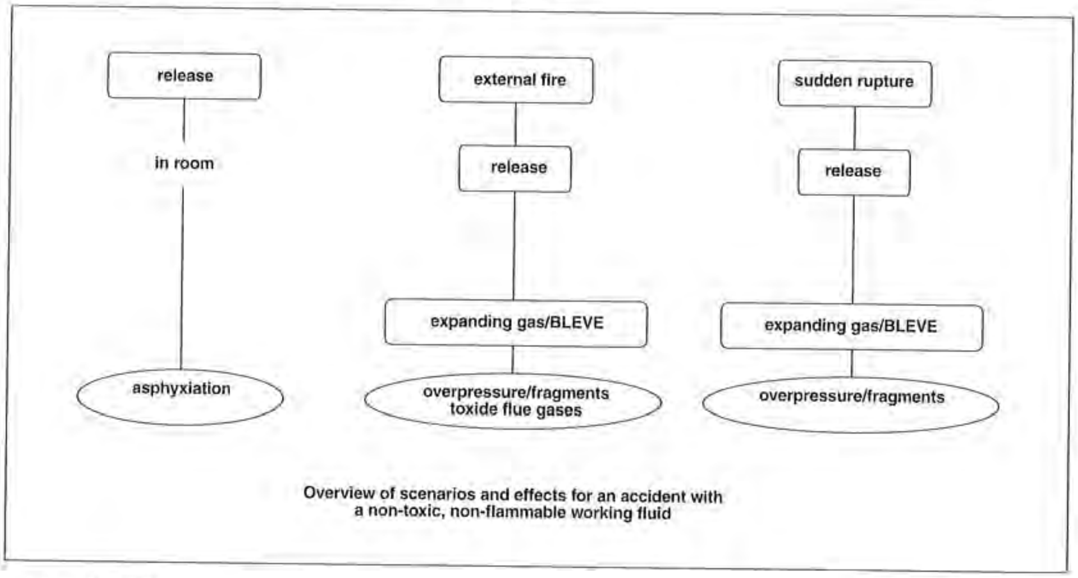
It is clear that the probit function derived will give only a very rough estimate of the effect on people as it is based solely on lethality. The result should only be used with this in mind.

10. THE EFFECTS OF ACCIDENTS INVOLVING A NON-TOXIC, NON-FLAMMABLE WORKING FLUID

This chapter and the three which follow examine the effects of accidents involving four, typical working fluids, freon 22 (R22), propane (R290), ammonia (R717) and sulphur dioxide (R764), each of which is representative of its classification as defined by toxicity and flammability.

Figure 10.1 gives an overview of the scenarios and effects associated with accidents involving a non-toxic and non-flammable working fluid (freon 22). The properties of this kind of working fluid mean that only a limited number of scenarios will give rise to the effects described.

Figure 10.1 Overview of scenarios and effects associated with an accident involving a non-toxic, non-flammable working fluid



☐ : events
◯ : effects
other : circumstances

10.1 Asphyxiation

A release of working fluid inside a room will result in asphyxiation effects if concentrations of the working fluid vapour are sufficiently high (20-30%). Figure 10.2 shows the evolution of this concentration in a room for both instantaneous and continuous releases, assuming some degree of ventilation (I = the number of total air changes per hour). The concentration is assumed to be homogeneous for both types of release. The evolution of the concentration as a function of time is exponential.

Where the release is instantaneous, the maximum concentration is found at the time of release and is a function of the amount released, the density of the working fluid vapour and the volume of the room. The calculations show that a maximum concentration of 20% can be expected where:

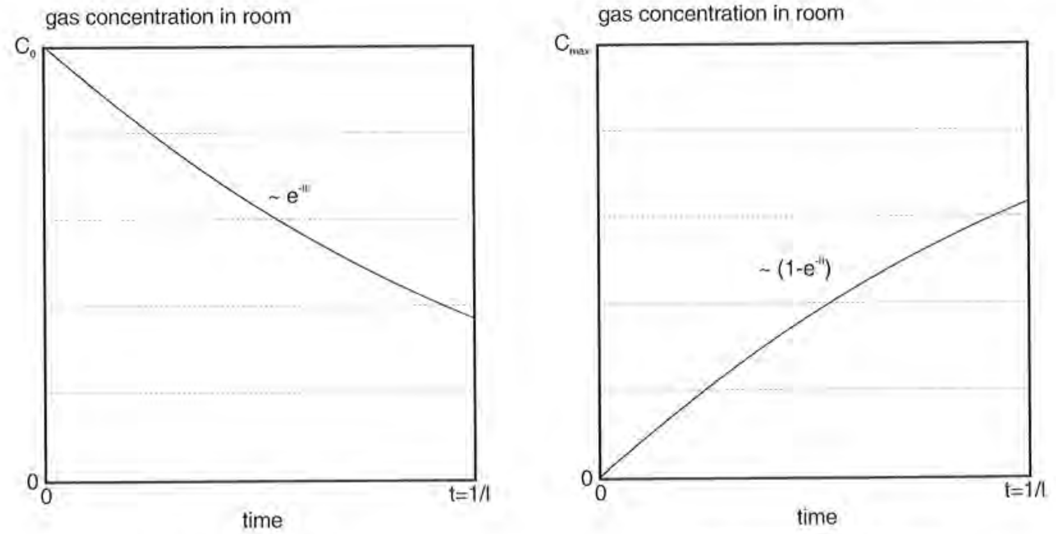
$$M = 0.75V \qquad (10.1)$$

where:

M = released mass (kg)
V = volume of chamber (m^3)

The density of R22 has been assumed in Formula 10.1 but, as most other working fluids in the non-toxic and non-flammable group have higher densities, Formula 10.1 is conservative and can be used as a rule of thumb. For carbon dioxide (CO_2), however, half of the mass found from Formula 10.1 is sufficient to reach a maximum concentration of about 20%. Exposure to this concentration may result in death within several minutes.

Figure 10.2 Evolution of the gas concentration in a room



gas concentration in room

gas concentration in room

Where the release is continuous, the concentration increases with time and is a function of the release rate, the density of the vapour and the ventilation rate. If no ventilation is assumed, the concentration in the room will increase proportionally with time until a pure R22 atmosphere is reached. A maximum concentration of 20% (R22) can be expected after 10 minutes of release where:

$$m = 1.2 \times 10^{-3} V \qquad (10.2)$$

where:

m = release rate (kg/s)
V = volume of chamber (m^3)

For an air-change rate of 2 (i.e. the total content of the room is changed twice per hour), about 80% of the concentration which can be expected without ventilation is reached after 10 minutes. Formula 10.2 is a conservative estimate in that respect. For CO_2, only half the release rate used in Formula 10.2 is required to achieve the same effect.

From the moment the continuous release is stopped, the concentration will decrease in the same way as for an instantaneous release.

10.2 Toxic Flue Gases

If an external fire occurs and the refrigeration installation is within the fire, toxic flue gases may be generated as a result of the decomposition of the working fluid (and other burning materials) when heated.

The combustion process is very complex. The burning of products consisting of carbon, hydrogen and oxygen atoms results only in the formation of the relatively harmless products H_2O and CO_2. Combustion with too little air can also generate toxic carbon monoxide (CO). Those atoms that may give rise to toxic combustion gases and that are found in the working fluids of the group under study are chlorine (Cl), fluorine (F) and bromine (Br). The toxic products formed are hydrogen chloride (HCl), chlorine (Cl_2), carbonyl chloride ($COCl_2$), hydrogen fluoride (HF) and hydrogen bromide (HBr).

As the working fluids considered are non-flammable, decomposition can only be expected during exposure to higher temperatures. A distinction can be made between two scenarios.

- In the case of a small fire (or the initial phase of a large fire) in a room where an installation with a non-toxic, non-flammable working fluid is present, the working fluid will not be the source of the fire nor will it enhance the fire. If the installation is damaged and the released working fluid is exposed to high temperatures, toxic decomposition products may be formed. By that stage the smoke and radiated heat will make entrance to the room impossible. This means that, although toxic combustion products pose an additional danger for people in the room, the other effects of the fire will initially be more significant.
- In the case of a large fire where the flames are in the open air and the combustion products are directly dispersed within the environment, a plume will rise, enhancing the dispersion process. Toxic decomposition products of the non-flammable working fluid will form only a small proportion of the flue gases produced. The toxic products are unlikely to have an adverse effect under these circumstances.

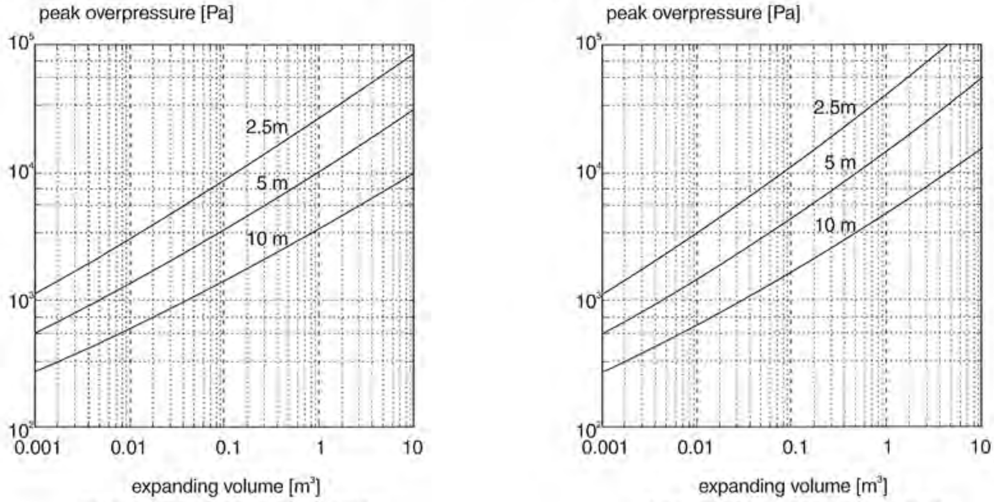
10.3 Overpressure

If an installation is exposed to excessive heat, failure of the exposed parts can be expected. Depending on the circumstances, the installation component, the working fluid etc, failure will result from an excessive overpressure and/or the loss of strength of the component. A pressure wave and fragments can be generated in the case of sudden component failure, particularly where the component involved is a vessel.

Any estimate of the peak overpressure in the pressure wave is based on the amount of expansion energy released. This in turn depends mainly on the scenario of the failure and the amount and phase of the working fluid that expands.

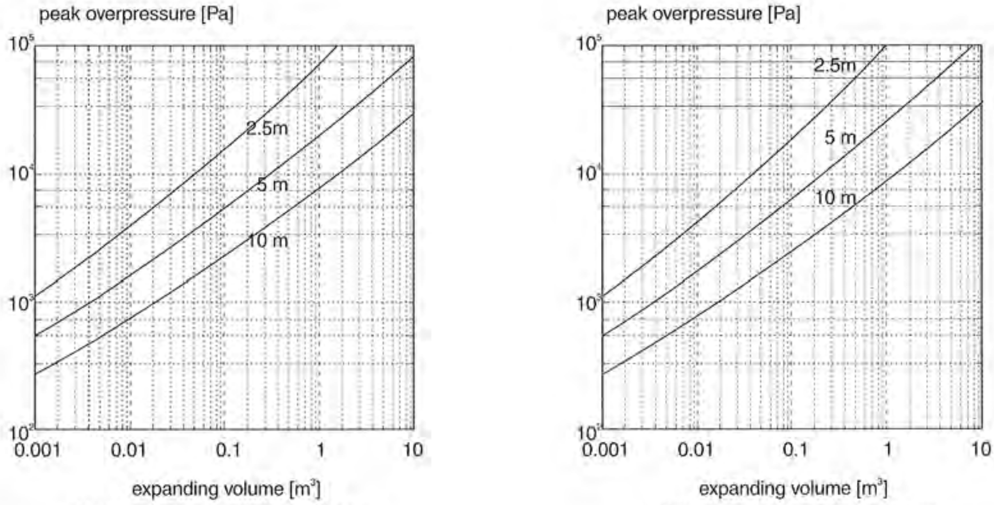
Figure 10.3 shows the maximum peak overpressure for the sudden release of a gas phase. The expansion is assumed to be isentropic between the pressure at the moment of release and the pressure after expansion (atmospheric). Ideal gas behaviour is assumed. The property of the gas is expressed by the ratio of the heat capacity at constant pressure to that at constant volume (c_p/c_v). The assumed ratio is 1.1. For gases with a higher ratio the results shown are conservative. A ductile rupture is assumed (Section 9.3.1). The maximum peak overpressure is given at distances of 2.5, 5 and 10 m from the vessel. The expansion is assumed to be unobstructed and at ground level (near a reflecting wall). An estimate of peak overpressure can easily be made from Figure 10.3.

Figure 10.3 Peak overpressure from expanding gas phase



initial expansion pressure = 5 barg

initial expansion pressure = 10 barg



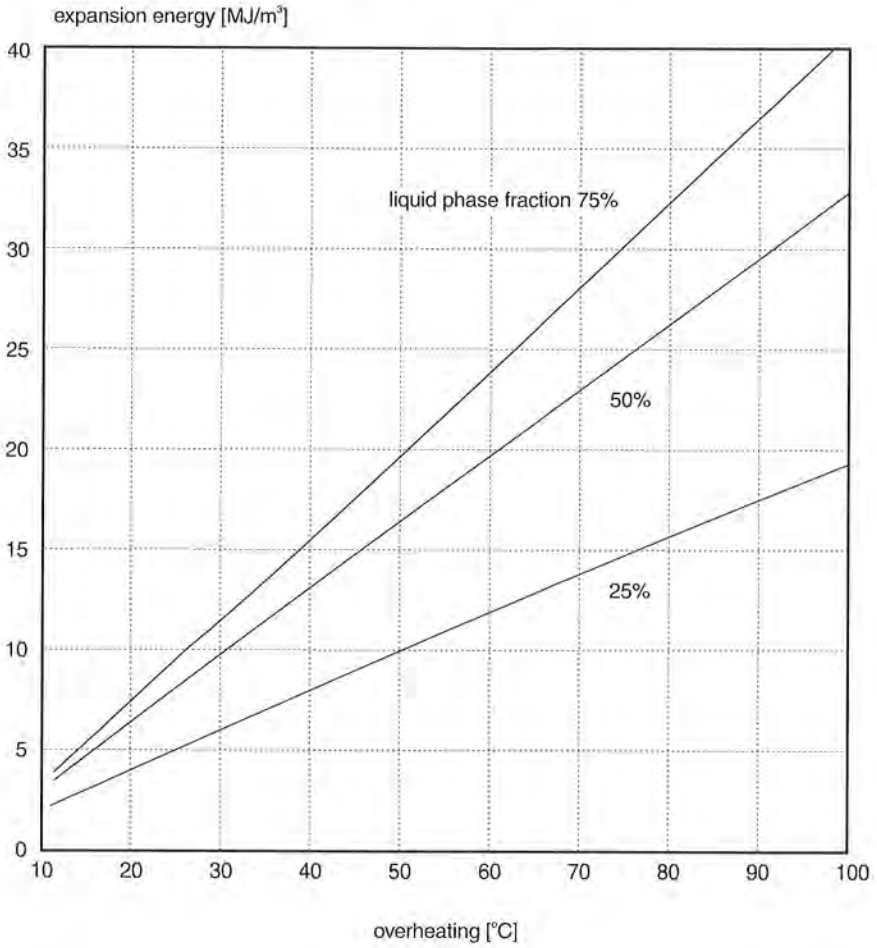
initial expansion pressure = 20 barg

initial expansion pressure = 30 barg

The same calculation procedure can be used for an expanding liquid phase, i.e. an isentropic expansion of the liquefied working fluid is assumed. The peak overpressure is then calculated from this expansion energy.

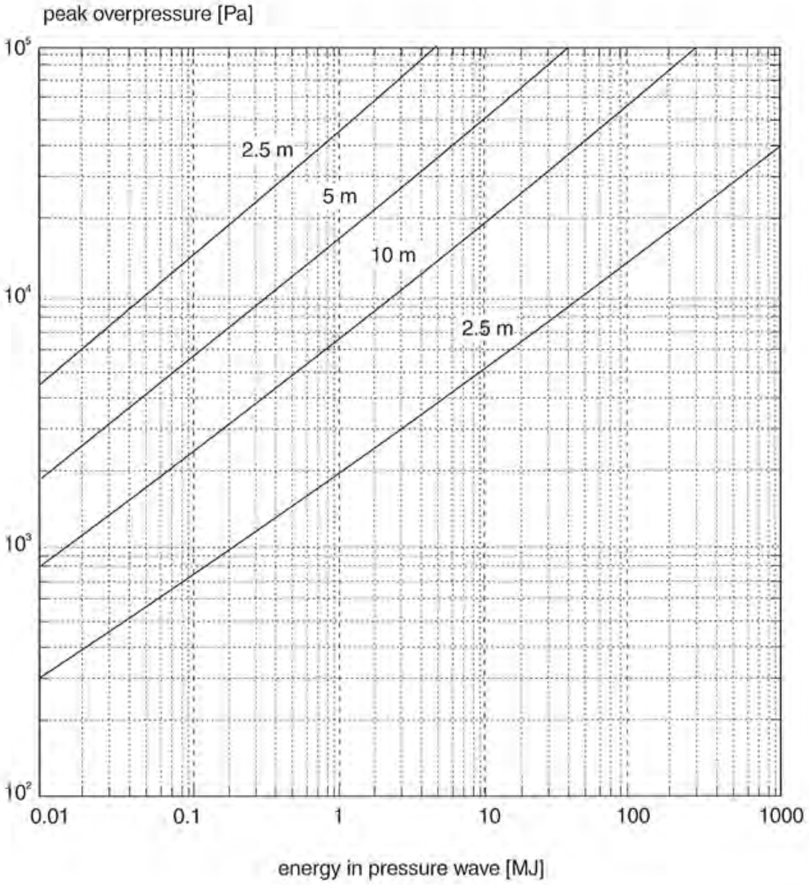
In order to determine the expansion energy the properties of the working fluid must be known. The isentropic expansion energy for 1 m^3 of R22 can be deduced from Figure 10.4 as a function of the liquefied phase content and the degree of overheating (the difference between the temperature of the fluid at the time of release and its atmospheric boiling point). The total expansion energy is calculated by multiplying the expansion energy derived from Figure 10.4 by the contents of the vessel (m^3).

Figure 10.4 Isentropic expansion energy for liquefied R22



For a ductile rupture, 40% of the isentropic expansion energy can be assumed to be in the pressure wave (Section 9.3.1). If the expansion occurs near a reflecting surface this can be taken into account by approximately doubling the expansion energy in the pressure wave before determining the peak overpressure from Figure 10.5.

Figure 10.5 Peak overpressure as a function of the energy in the pressure wave



10.4 Fragments

The formation of fragments and their velocity which turns them into missiles depends on the specific circumstances. A rough estimate of the maximum initial velocity can, however, be made, based on:

- that part of the expansion energy that is found as kinetic energy in the fragments (Section 9.3.1);
- the total accelerated mass.

The expansion energy for an isentropic expansion of the gas phase can be found using Figure 10.6. For the expansion of a liquefied gas (R22) Figure 10.4 must be used.

In the case of a ductile rupture 60% of the expansion energy can be assumed to be found as kinetic energy in the fragments. The maximum initial velocity of the fragments can be estimated from Figure 10.7 when the kinetic enegy and the total accelerated mass are known. The maximum distance that a missile theoretically can reach is equal to the square of the velocity divided by the gravitational acceleration if only the gravitational force is taken into account. The distance will, in that case, be largely overestimated. References [56] and [66] can be used for an estimate which takes into account drag and lift forces.

Figure 10.6 Isentropic expansion energy for an expanding gas phase

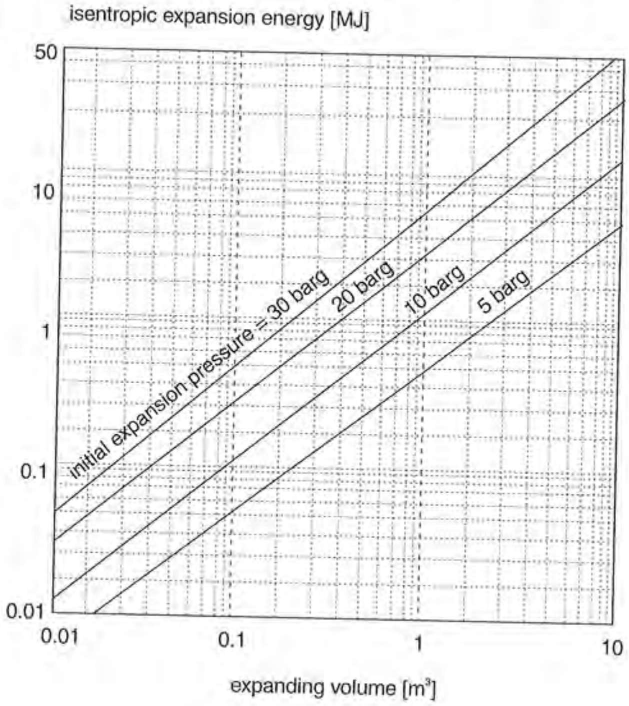
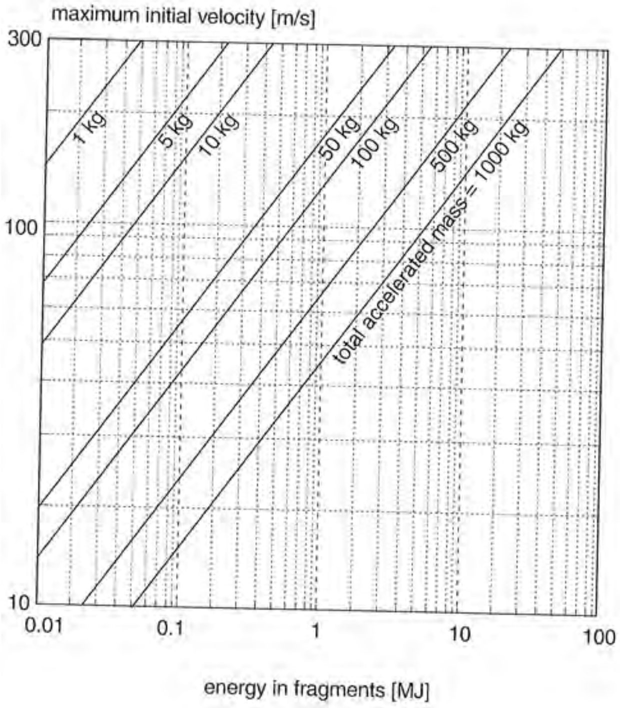


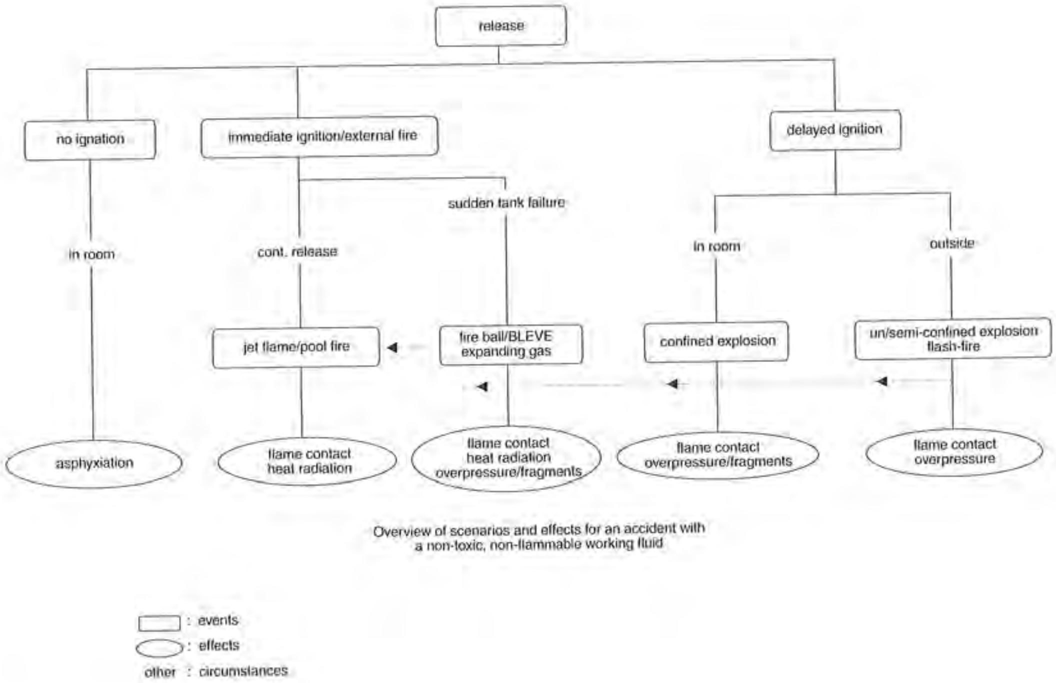
Figure 10.7 Maximum initial velocity of fragments



11. THE EFFECTS OF ACCIDENTS INVOLVING A NON-TOXIC, FLAMMABLE WORKING FLUID

Figure 11.1 gives an overview of the scenarios and effects associated with accidents involving a non-toxic but flammable working fluid (propane). The dashed line with the arrows indicates that, in the case of ignition (immediate or delayed), a jet flame or a pool fire can ultimately be expected. Because of the properties of this kind of working fluid, the hazards are mainly those relating to fire and explosion.

Figure 11.1 Overview of scenarios and effects associated with an accident involving a non-toxic, flammable working fluid



11.1 Asphyxiation

Reference is made to Section 10.1 where asphyxiation was discussed. It is clear that asphyxiation will only be relevant if ignition does not occur. As the density of the flammable, non-toxic working fluids is typically about half that of R22, the required released amount (or release rate) giving asphyxiation effects is determined by taking half of the masses mentioned in Formulas 10.1 and 10.2.

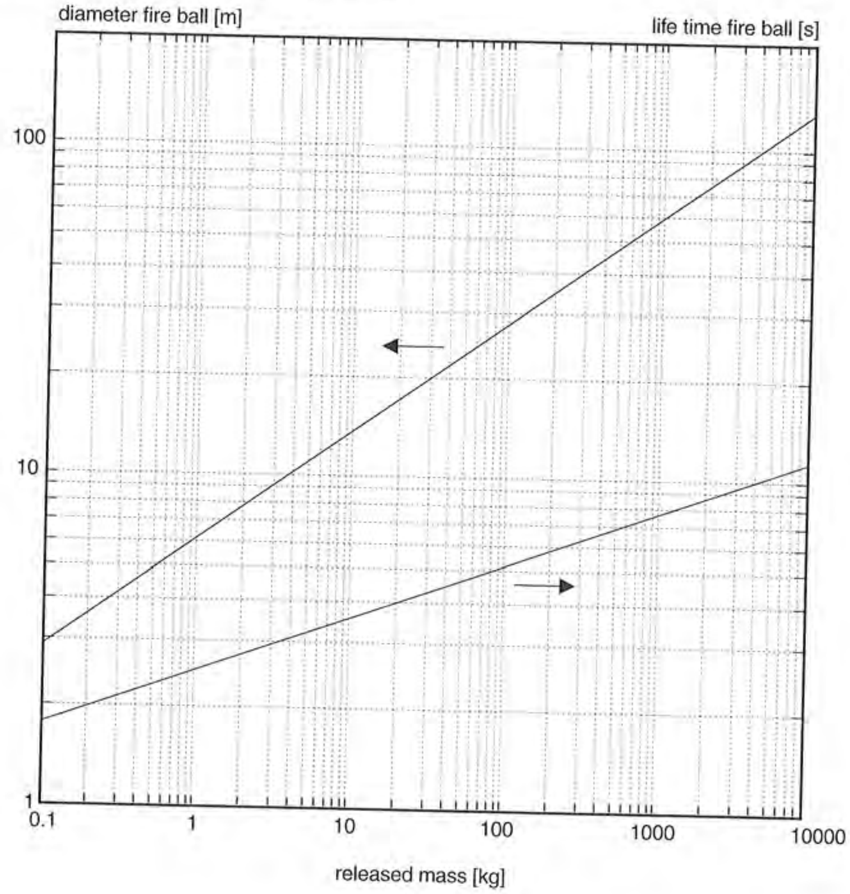
11.2 Heat Radiation/Flame Contact From a Fire-Ball

An external fire or other ignition source may result in a fire. A distinction is made between a sudden tank failure and other scenarios.

The sudden failure of a vessel, releasing the liquefied flammable working fluid contained within it, can give rise to a fire-ball.

In Figure 11.2 the maximum diameter and lifetime of a fire-ball are given as a function of the released mass. Even where only small amounts of mass are involved the maximum fire-ball diameter attains several metres. The lifetime is, however, always relatively short. This implies that the effects are most likely to be experienced through flame contact. Only where large amounts of fluid are released will heat radiation also become important. A fire-ball grows with time and so the maximum diameter is not attained immediately. During this growth the fire-ball will rise. The maximum diameter can be taken as an estimate of the distance over which the relevant effects can be expected.

Figure 11.2 Characteristics of a fire-ball

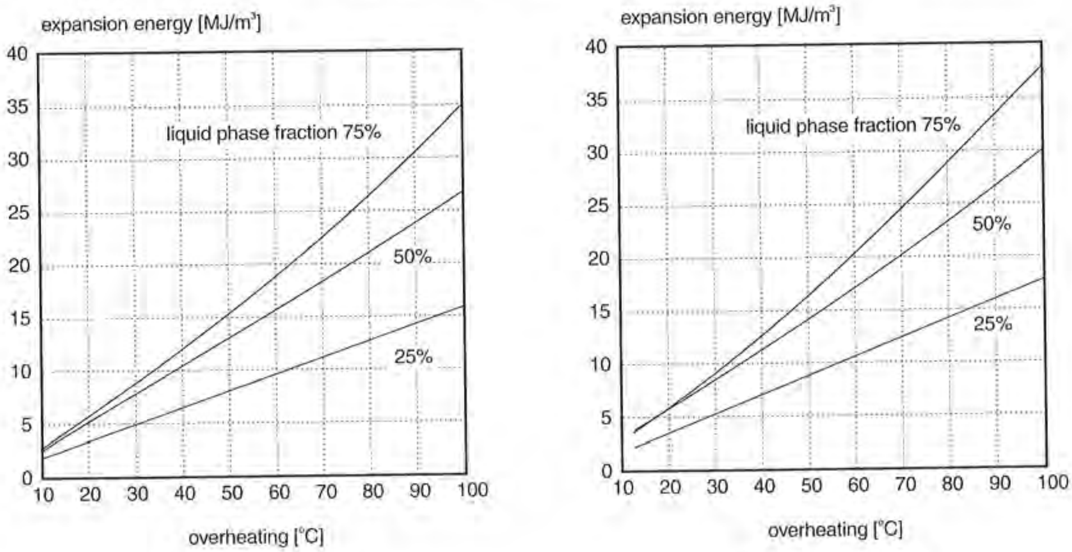


11.3 Overpressure From a BLEVE

The sudden release of a liquefied working fluid under pressure will also give rise to a pressure wave. This phenomenon has already been discussed in Section 10.3. Figure 11.3 gives the expansion energy for 1 m^3 of both n-butane and propane as a function of the liquefied phase fraction (vol %) and the degree of overheating. The total expansion energy is calculated by multiplying the energy derived from Figure 11.3 by the contents of the vessel (m^3).

The peak overpressure can be determined using Figure 10.5, taking into account the type of rupture (for a ductile rupture 40% of the expansion energy is expected to be found in the pressure wave) and the presence or otherwise of a reflecting surface (which doubles the energy in the pressure wave).

Figure 11.3 Expansion energy for liquefied n-butane and propane



expansion of n-butane

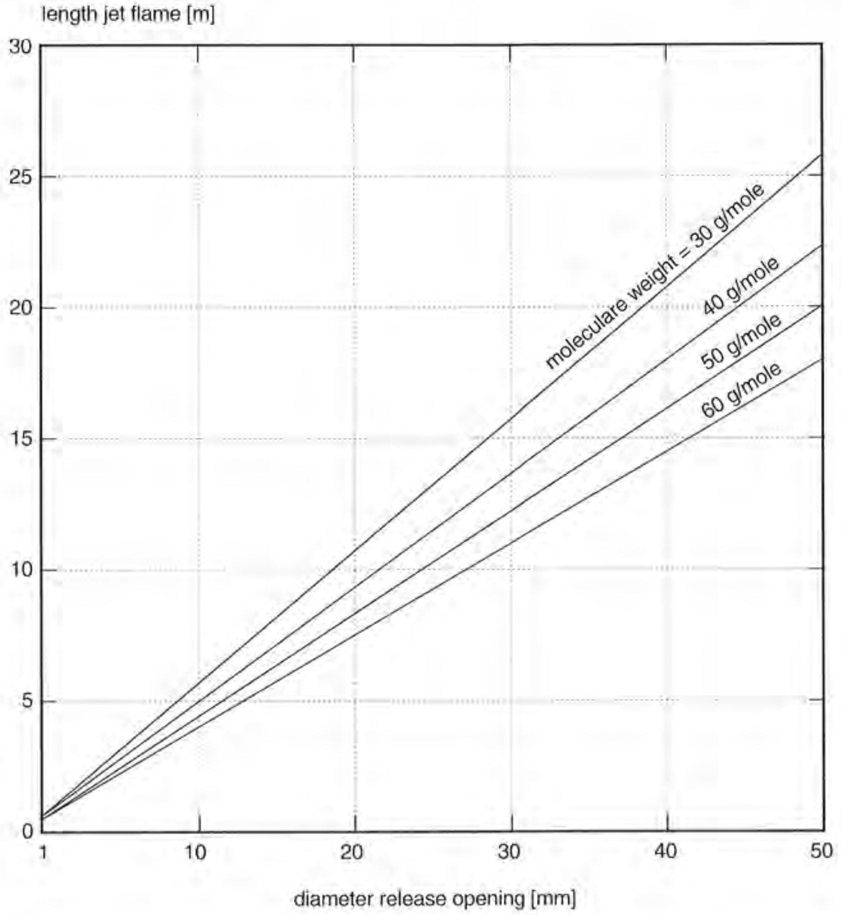
expansion of n-butane

For the sudden rupture of a tank filled with a gas phase, the previous results given in Section 10.3 can be used.

11.4 Heat Radiation From a Jet Flame

The ignition of a continuous release of a flammable working fluid results in a jet flame. The effects associated with heat radiation or flame contact can be expected. For turbulent flames the flame length does not depend on the release velocity and, in Figure 11.4, this flame length is given as a function of the diameter of the release opening and the molecular weight of the flammable working fluid. The results are also valid for a lean flammability limit of 2%. For higher lean flammability limits the results in Figure 11.4 are conservative.

Figure 11.4 Flame length of a turbulent jet flame (lean flammability limit = 2 vol %)



For small jet flames the effects associated with flame contact are to be expected first. The effects of exposure to heat radiation will only be relevant for large jet flames. The heat radiation levels for a vertical jet flame with a release opening of 50 mm (at ground level) are given in Figure 11.5. The emittance fraction is taken to be 0.3. With respect to the orientation of the release it is obvious that, if the vertical jet flame is tilted by a cross-wind, this will result in higher heat radiation levels downwind[1]

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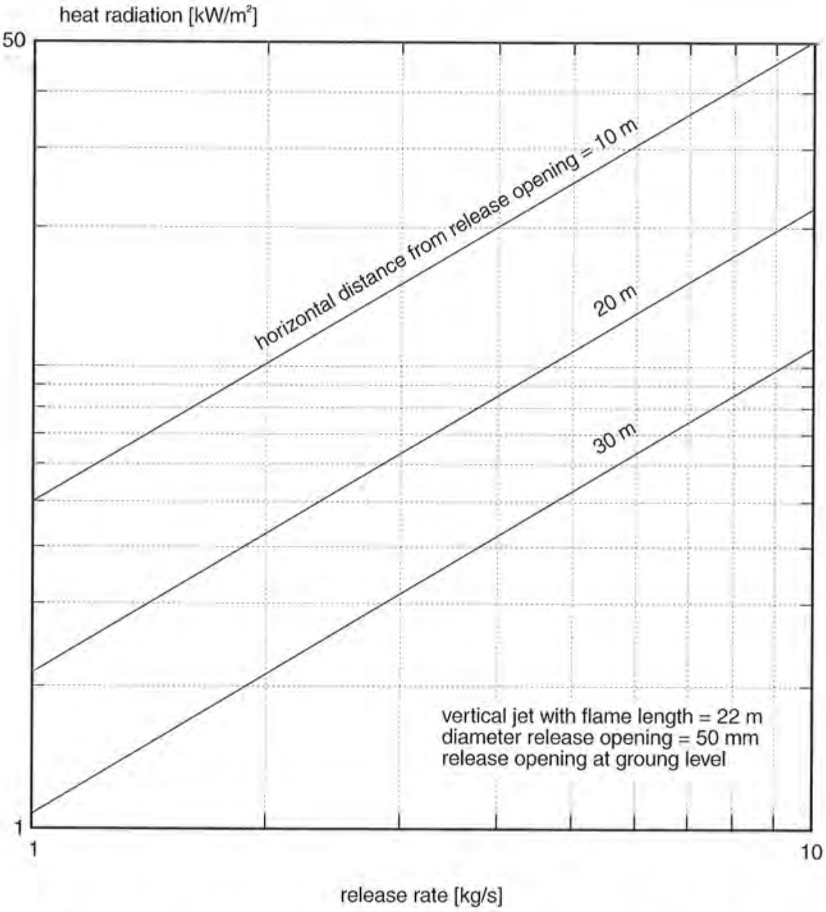
[1] In that case specific calculations can be executed using the calculation program provided

Figure 11.5 Heat radiation from a vertical jet flame

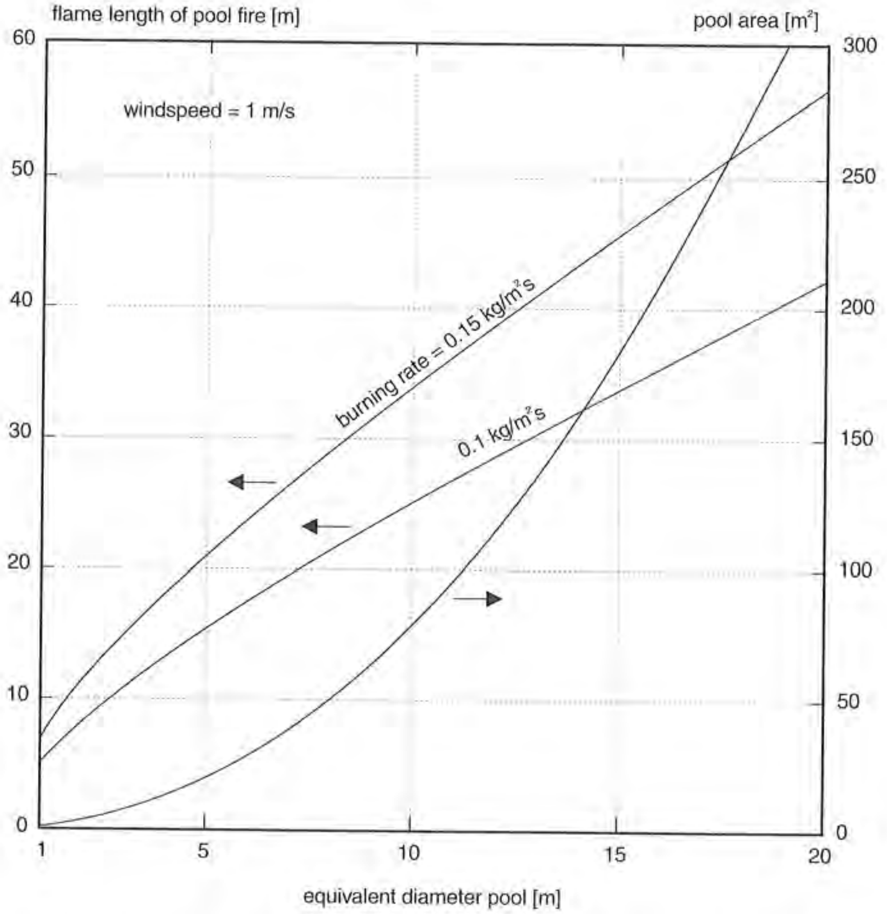


The impact of a jet flame on other installations is a significant factor with respect to the escalation of an accident.

11.5 Heat Radiation From a Pool Fire

The ignition of the liquid pool formed by a flammable working fluid results in a pool fire. The flame is modelled as a cylinder. In Figure 11.6 the flame length is given as a function of the equivalent diameter of the pool. If the pool is not round, this figure also helps to establish the equivalent diameter from the known pool area. With respect to the density of the working fluid vapour, the results given are conservative. The burning rate of propane at the liquid surface is about 0.13 kg/m^{2}s.

Figure 11.6 Flame length for a pool fire



The radiation of a pool fire is calculated from the maximum heat radiation at the flame surface. Figure 11.7 presents a general correlation by which the heat radiation at the flame surface can be determined for hydrocarbon pool fires (only valid for liquid pools on land).

Figure 11.8 can be used to determine the heat radiation at distances of 10, 20 and 50 m from the centre of the pool. A heat radiation of 10 kW/m^2 at the flame surface is assumed. If the maximum heat flux at the surface is, for example, 70 kW/m^2 (from Figure 11.7), then the result obtained from Figure 11.8 should be multiplied by 7 to obtain the heat radiation in the environment.

Figure 11.7 Maximum heat radiation at flame surface

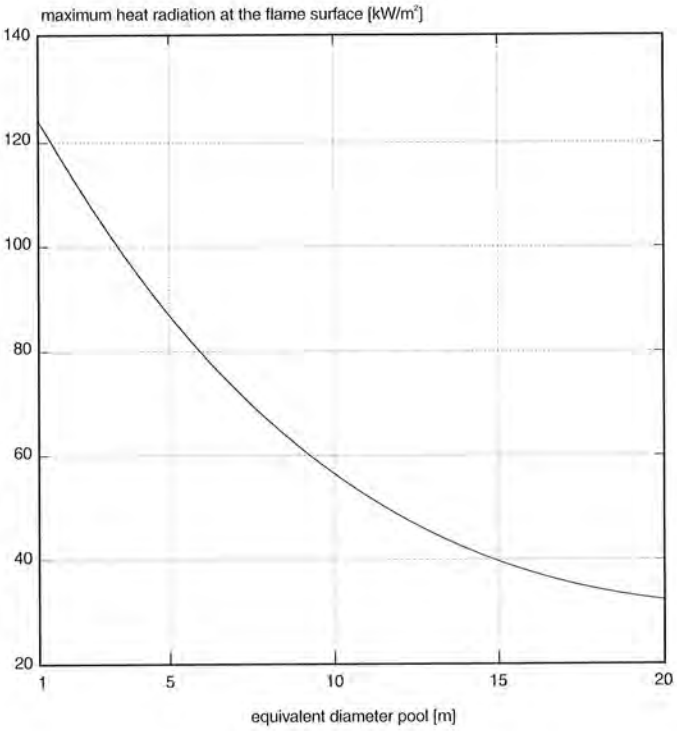


Figure 11.8 Heat radiation from a pool fire

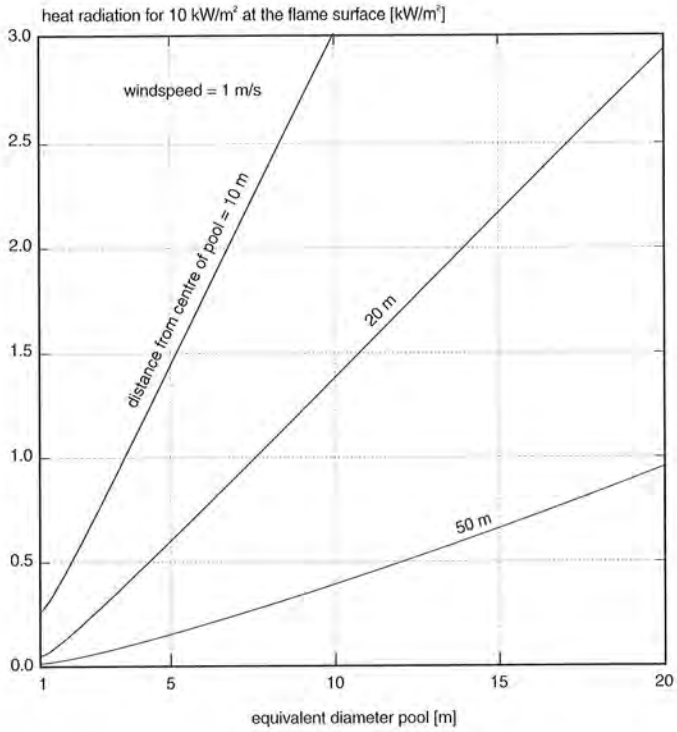
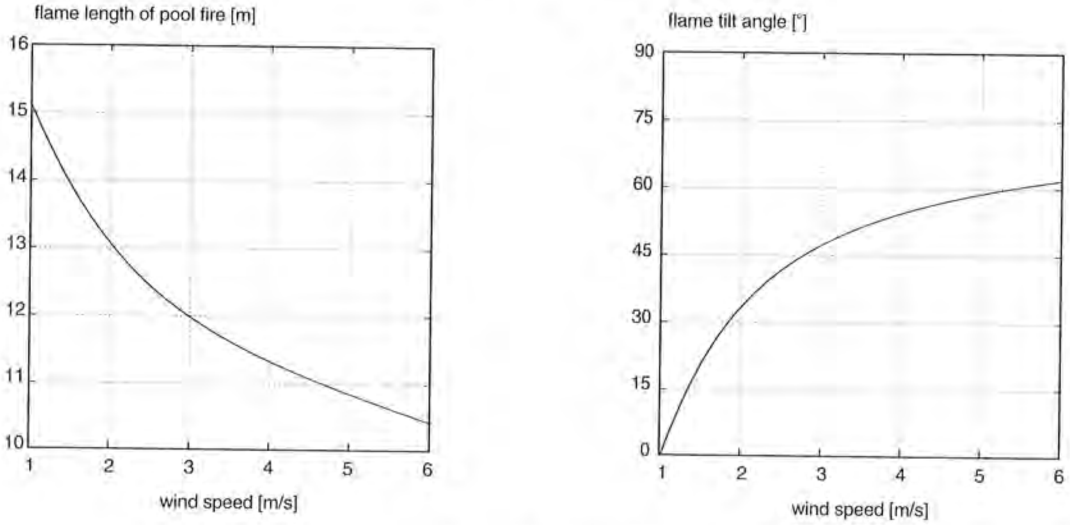


Figure 11.9 illustrates the influence of the wind speed on the flame length as well as on flame tilt (the flame tilt angle is measured from the vertical).

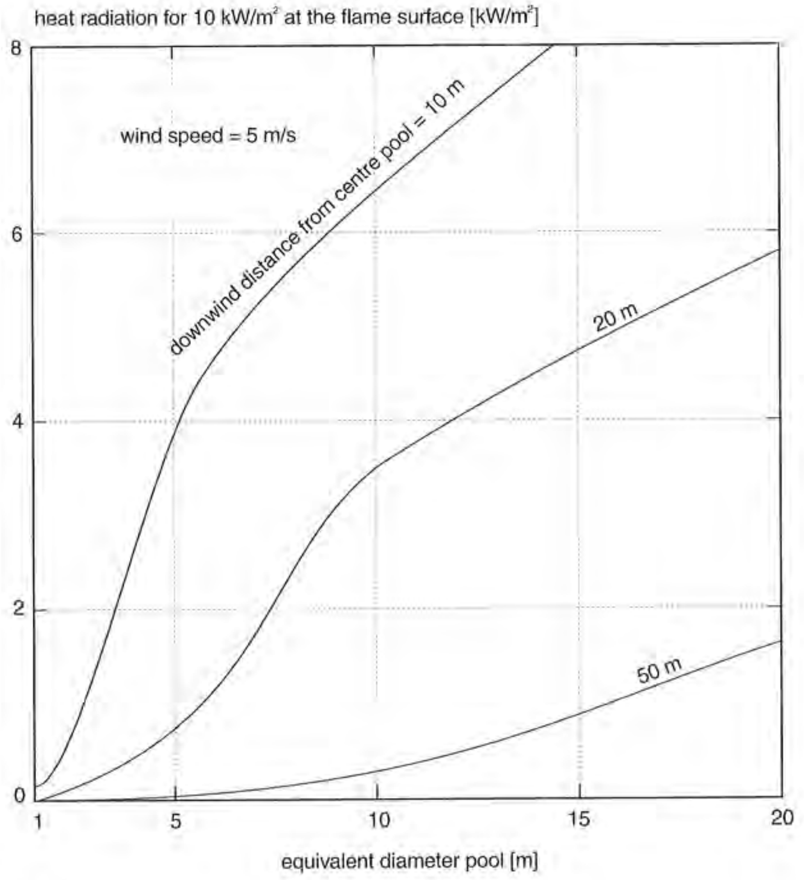
Figure 11.9 Flame length and tilt for a pool fire



burn rate = 0.1 kg/m²s
diameter pool = 5 m

At higher wind speeds the flames will be tilted, and downwind heat radiation levels will increase considerably. Figure 11.10 illustrates the downwind heat radiation levels assuming a wind speed of 5 m/s.A comparison of Figures 11.8 and 11.10 demonstrates that the increase in the heat radiation level downwind cannot be ignored. The upwind heat radiation levels, however, will be lower than those illustrated in Figure 11.8.

Figure 11.10 Heat radiation from a pool fire (downwind)

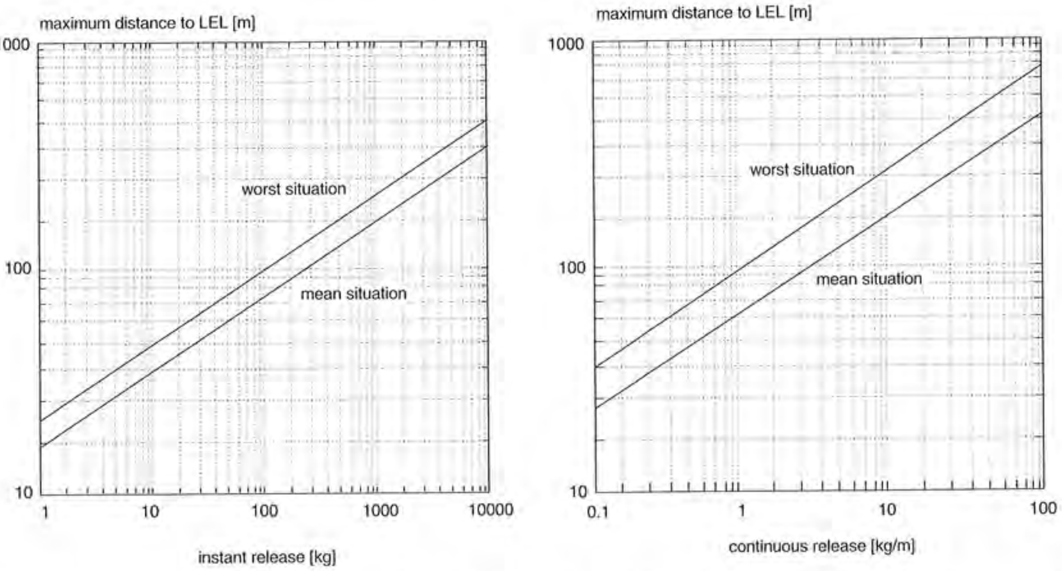


11.6 Flame Contact From a UVCE

If a flammable cloud is ignited a flash fire or explosion will result. With respect to the effects of flame contact, the area where the concentration of flammable vapour is beyond the LEL is assumed to be relevant. The maximum distance over which the LEL can be found is therefore estimated.

Figure 11.11 gives the maximum (downwind) distance over which the LEL can be expected in the case of both an instantaneous and a continuous release of propane. The working fluid is assumed to be liquefied on release. The results provide an estimate of the downwind distance over which the LEL can be expected for a heavy gas dispersion. For n-butane the maximum distance for the mean situation is nearly the same. For the worst dispersion situation the maximum error is 4%.

Figure 11.11 Dispersion of the flammable working fluid vapour of propane



Where the release is instantaneous it is clear that the LEL will only exist for a short time at its maximum distance.

Where the release is continuous, the maximum distance is only reached when the release occurs over a long period of time.

The width of the cloud formed at equilibrium is estimated to be about one order of magnitude smaller than its length.

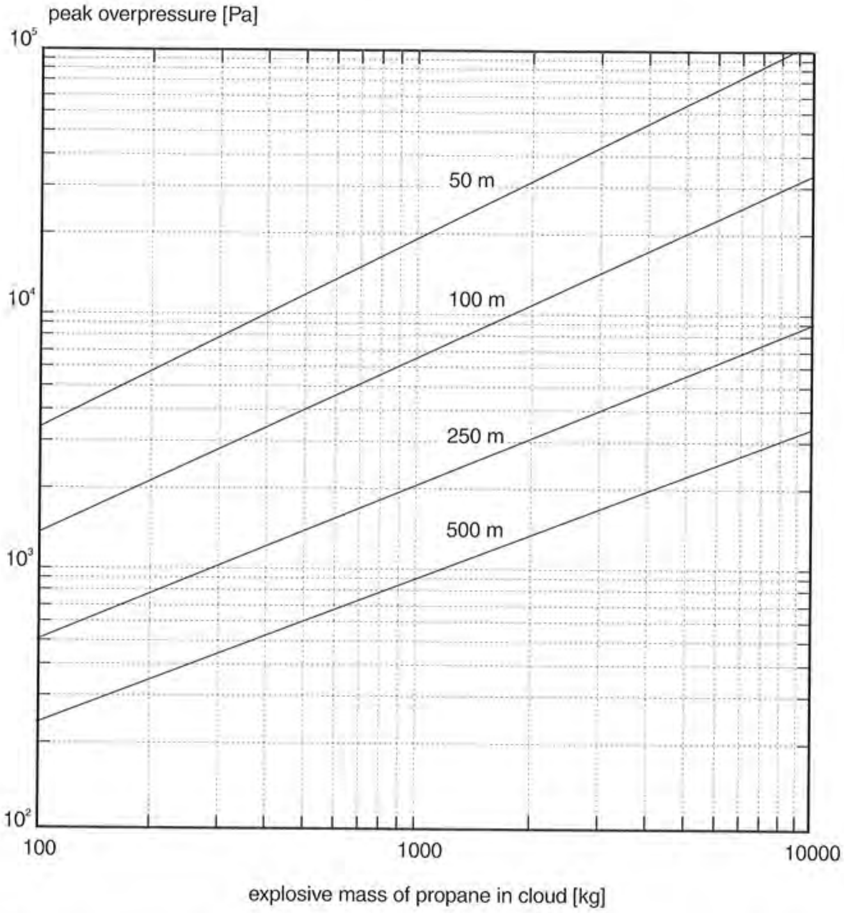
11.7 Flame Contact From a Confined Explosion

In the case of a confined explosion, flame contact can first be expected within the confined space in which the flammable mixture is present. If part of the room fails first and a venting of the explosion occurs, flames will also be 'vented' through the opening. In general, however, the effects will depend on specific circumstances.

11.8 Overpressure From a UVCE

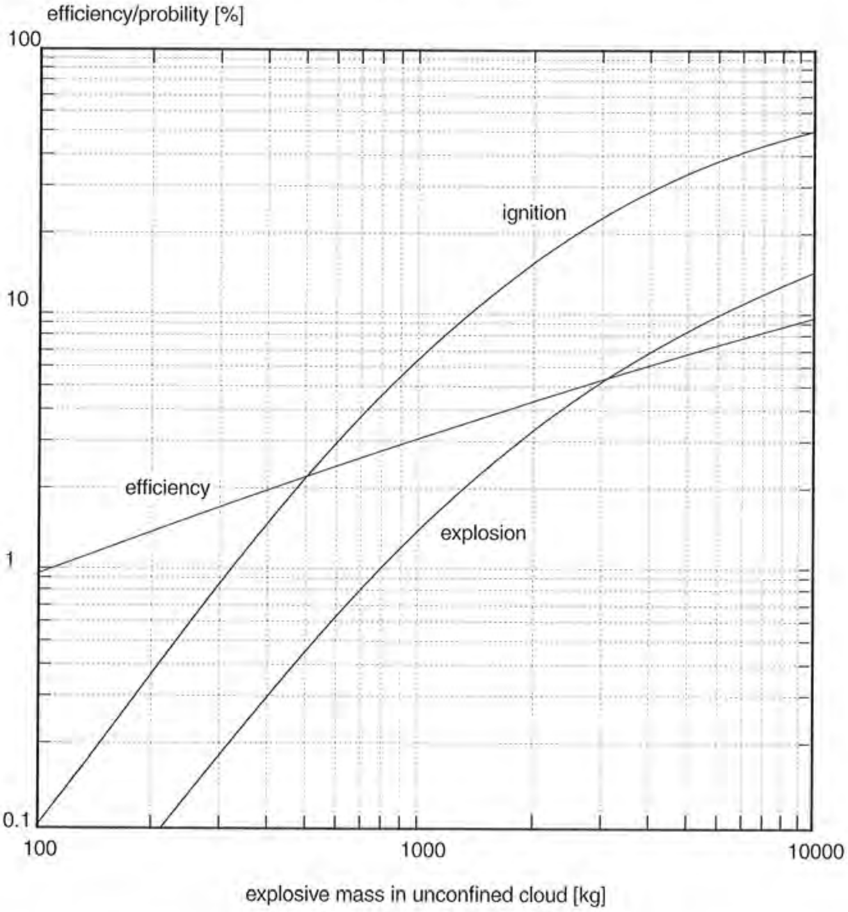
The overpressure from a UVCE can be estimated from Figure 11.12, given the amount of propane in the cloud between the explosion limits.

Figure 11.12 Overpressure from a UVCE



The efficiency assumed for the calculation of the overpressure in Figure 11.12 is taken as a function of the explosive mass in the cloud. This efficiency of explosion is shown in Figure 11.13, together with the ignition probability and the explosion probability, both given as a function of the explosive mass based on historical data.

Figure 11.13 Efficiency of the explosion for a UVCE



For a cloud that is semi-confined and of which only the confined part is involved in an explosion, the overpressure is found by taking only the latter part of the explosive cloud mass into account. The accurate determination of this amount requires sound judgement.

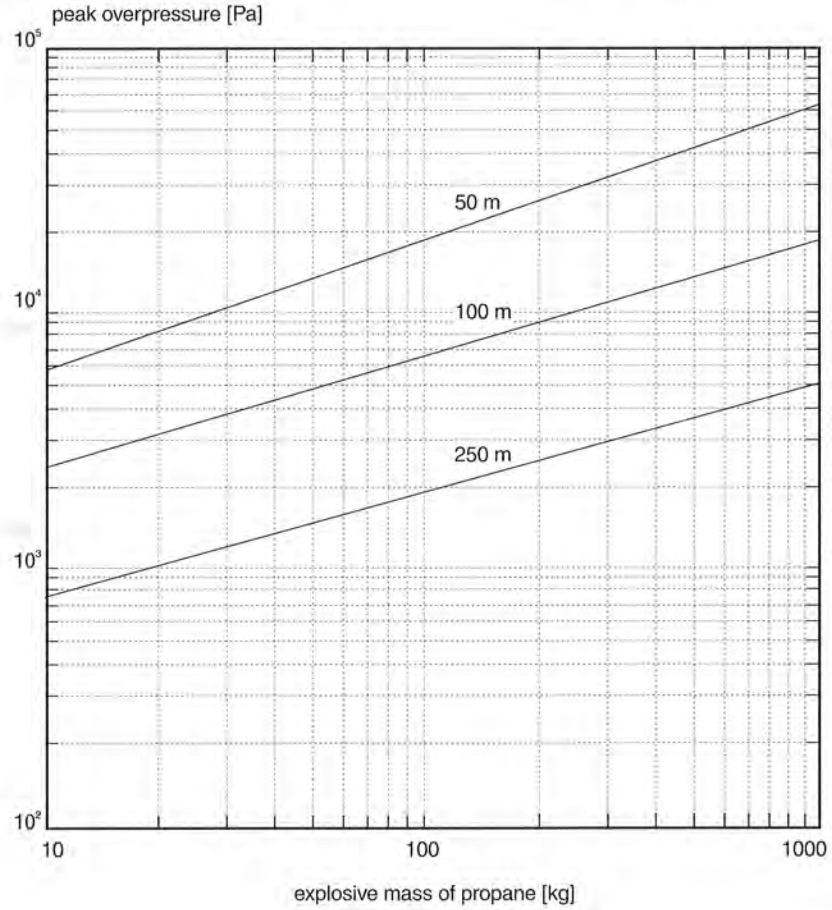
The largest explosive clouds can be expected with the sudden release of a liquefied gas. The explosive mass in the vapour cloud will first be small as most of the vapour is above the UEL. Dilution of the cloud will result in an increase in the explosive mass until a maximum is reached. When no vapour is left at concentrations above the UEL, further dilution will decrease the explosive mass in the cloud. The maximum figure can be estimated at between one-third and two-thirds of the initial released mass (depending on local circumstances such as wind speed). The centre of this cloud can be located half-way between the source of the release and the maximum distance where the LEL can be found.

11.9 Overpressure From a Confined Explosion

The explosion of a flammable mixture in a room is a confined explosion. The overpressure that can be generated in the environment when the room fails is very difficult to estimate because it will depend very much on specific circumstances such as the strength of the room.

It is, however, possible to make a *rough* estimate of the peak overpressure from Figure 11.14, assuming a maximum explosion efficiency of 40%.

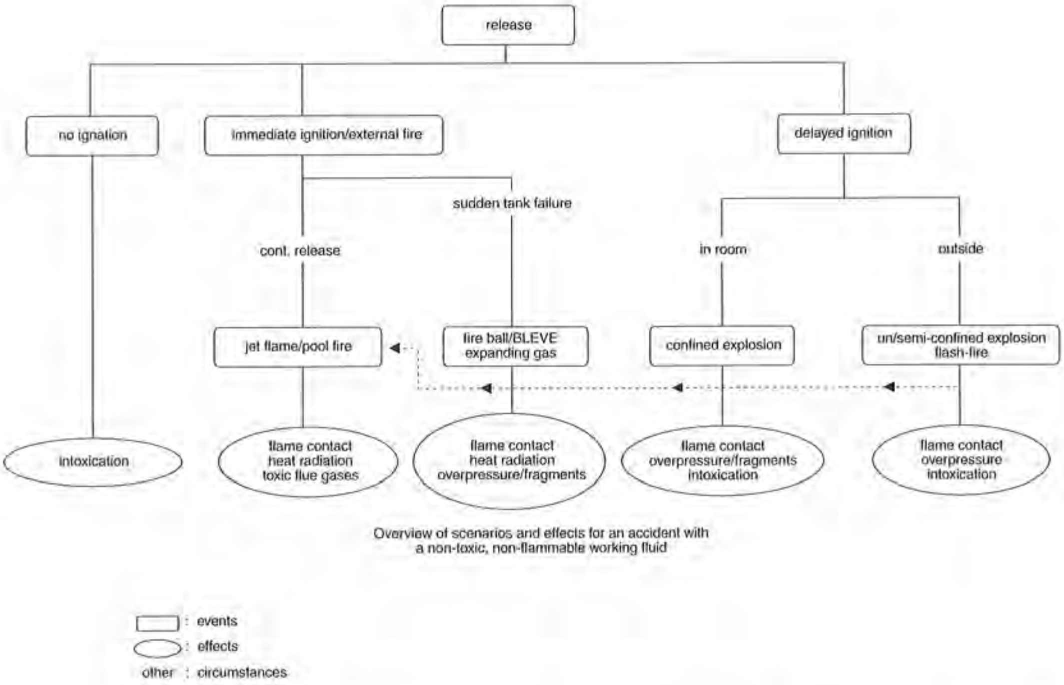
Figure 11.14 Overpressure for an explosion with 40% efficiency



12. THE EFFECTS OF ACCIDENTS INVOLVING A TOXIC, FLAMMABLE WORKING FLUID

Figure 12.1 give an overview of the scenarios and effects associated with accidents involving a toxic, flammable working fluid (ammonia). The dashed line with the arrows indicates that, in the case of ignition (immediate or delayed), a jet flame or a pool fire can ultimately be expected. The hazards are related both to intoxication and to fire and explosion. It is clear from earlier sections of this report that ammonia is not a very representative example of its group in terms of fire and explosion hazards. However, as these effects have already been discussed, greater importance is attached in this chapter to its toxicity.

Figure 12.1 Overview of scenarios and effects associated with an accident involving a toxic, flammable working fluid



If the effects listed in Figure 12.1 are compared with those for the non-toxic, flammable working fluids (Figure 11.1), a number of differences can be identified.

- When no ignition occurs exposure to the working fluid vapour gives rise to intoxication effects rather than to asphyxiation. As intoxication occurs at lower concentrations than asphyxiation, it can also be experienced outside, in the open air.
- If a fire occurs, toxic flue gases can be expected for those working fluids that contain atoms such as Cl.
- In the case of delayed ignition, the additional effects of intoxication can occur before ignition takes place.

For the fire and explosion effects, reference is made to the group of non-toxic, flammable working fluids discussed in Chapter 11. Only the differences which occur between the two groups are discussed further.

12.1 Heat Radiation/Flame Contact From a Fire-Ball

The results already obtained for the dimension and duration of a fire-ball (Figure 11.2) are also valid for the release of a toxic, flammable working fluid. However, as the combustion heat of these fluids is generally less than for the non-toxic, flammable working fluids, the radiated heat will also be less.
Table 12.1 details the heat of combustion for typical toxic, flammable working fluids. It shows that the heat of combustion for this type of working fluid is between 30% and 40% of the heat of combustion of propane. The maximum diameter of the fire-ball (a function of the amount of fluid involved) can still be taken as an estimate of the distance over which relevant effects can be expected.

Table 12.1 Heat of combustion for toxic, flammable working fluids

Fluid	Heat of combustion (propane = 100)
Ammonia (R7170)	40
Chloromethane (R40)	28
Methylformate (R611)	32
Chloroethane (R160)	41
Dichloroethane (R1130)	35

12.2 Heat Radiation From a Jet Flame

The length of a turbulent jet flame is determined by the diameter of the release opening and the molecular weight and lean flammability limit of the fluid.

The influence of the molecular weight on the flame length has already been shown in Figure 11.4. With the exception of ammonia, the molecular weight of the toxic, flammable working fluids is equal to or higher than that for the hydrocarbon flammable working fluids. This implies that the flame length will be equal or smaller for most of the toxic working fluids than for the flammable, non-toxic working fluids.

The lean flammability limit for the toxic, flammable working fluids is higher than the value of 2% given for propane. These lean limits are shown in Table 12.2. As the flame length is determined by the distance at which the lean flammability limit is found, higher lean limits result in smaller jet flames.

Table 12.2 Lean flammability limit of toxic, flammable working fluids

Fluid	Lean flammability limit (vol %)
Ammonia (R717)	15.3
Chloromethane (R40)	8
Methylformate (R611)	4.5
Chloroethane (R160)	3.7
Dichloroethane (R1130)	5.6

Not only the flame length will be smaller for the toxic, flammable working fluids, when compared with a propane jet flame. The lower heat of combustion and a smaller heat radiation fraction (Section 12.3 below) will, in addition, result in lower heat radiation levels.

12.3 Heat Radiation From a Pool Fire

Determining the heat radiation from a pool fire requires knowledge of the pool diameter, the flame height and the maximum heat radiation at the flame surface. Table 12.3 shows a comparison of these parameters for toxic, flammable working fluids and propane. A pool diameter of 1 metre is assumed [57].Values for R1130 were not found.

Table 12.3 clearly shows that the flame length and especially the maximum heat radiation at the flame surface are much smaller than the equivalent values for propane. The effects of heat radiation will therefore be less severe for the toxic, flammable working fluids. The low emissivity of the flames also results in a smaller re-radiation of heat to the liquid of the pool. This helps to explain the lower burning rates and flame lengths.

Table 12.3 Pool fire characteristics for toxic, flammable working fluids

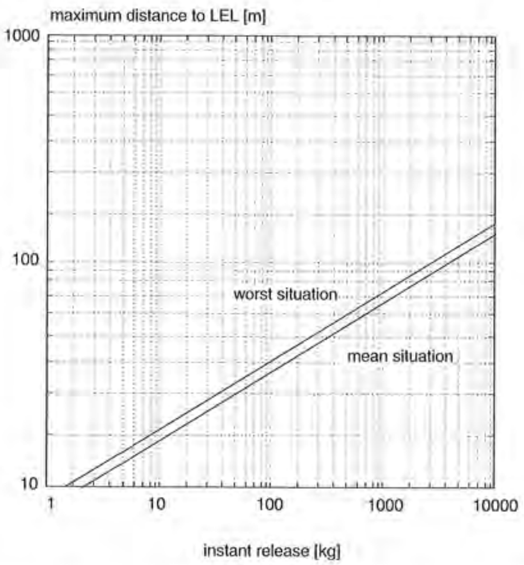
Fluid	Flame height/diameter pool (propane = 100)	Maximum heat radiation (propane = 100)
Propane	100	100
Ammonia (R717)	31	18
Chloromethane (R40)	96	15
Methylformate (R611)	46	19
Chloroethane (R160)	60	29

12.4 Flame Contact From a UVCE

The relevant factor with respect to the effects of flame contact in the case of a flammable cloud being ignited is the area over which the concentration of the flammable vapour is above the LEL.

As already shown in Table 12.1, the LEL is generally higher than that for propane. This implies that the maximum distance over which the LEL can be expected will be smaller. In the case of ammonia, which has a high LEL, the flammable cloud will be very much smaller. If it is assumed that ammonia is released from a pressurised vessel so that it cools down when expanding and the initial dispersion is a heavy gas dispersion, the relevant situations are shown in Figure 12.2.

Figure 12.2 Dispersion of ammonia vapour



The graphs in Figure 12.2 have been derived in the same way as those in Figure 11.11 for propane. The maximum (downwind) distance to the LEL is about two times smaller for the dispersion of ammonia than for the dispersion of propane. Where continuous release is involved, the difference between the mean and worst dispersion situations is small.

It should also be remembered that, particularly for ammonia, the ignition of the vapour requires a much higher ignition energy than, for example, for propane.

For working fluids with an atmospheric boiling point above ambient temperature (R30, R1130, R611), not all the released fluid will be in the gas phase (as assumed for the dispersion of ammonia). A liquid pool will be formed, and the dispersion calculation must take into account the evaporation rate from this pool[1].

12.5 Overpressure From a UVCE

The overpressure from a UVCE can be deduced from Figure 11.12 in which a flammable cloud of propane is assumed. The explosive strength is proportional to the heat of combustion of the fluid involved. The overpressure from a UVCE of a fluid other than propane is found by taking into account the difference in the heat of combustion. For a cloud of ammonia, which has a heat of combustion that is about 40% of that for propane, 2.5 times the explosive mass will be needed, compared with propane, to obtain the same peak overpressure in the blast.

12.6 Overpressure From a Confined Explosion

In the case of a confined explosion, the higher explosion limits of the toxic, flammable working fluids can result in higher explosive concentrations in a room. As discussed above (Section 12.5), the heat of combustion must be taken into account. Figure 11.14 can be used in the same way as described above for Figure 11.12.

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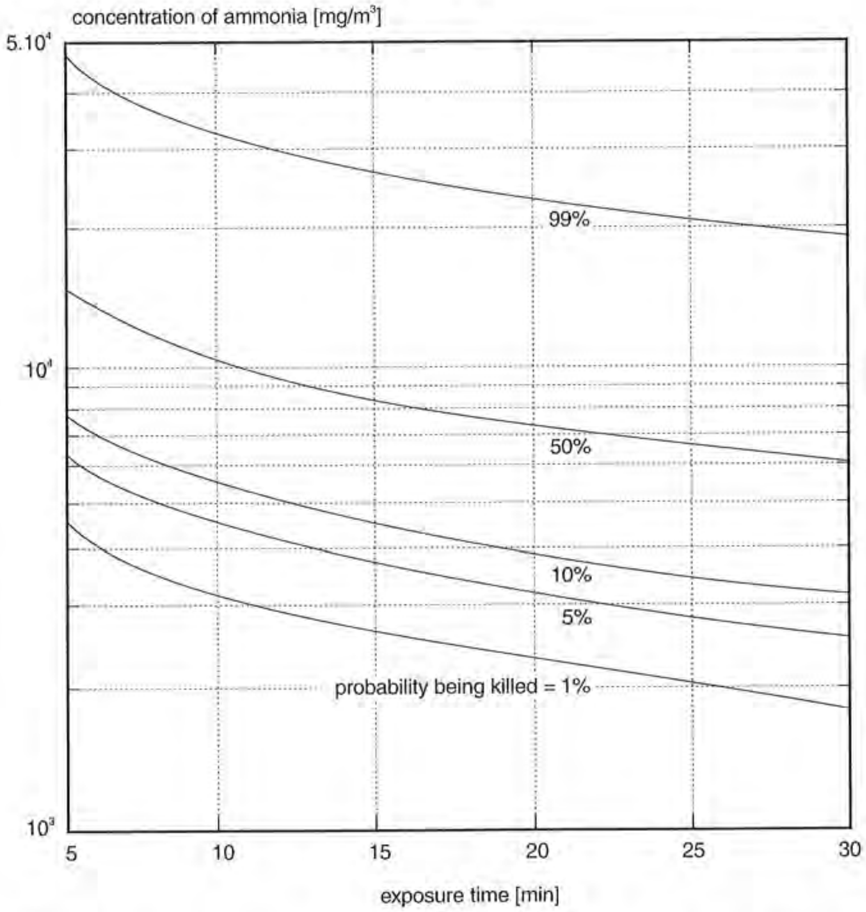
[1] The evaporation rate can be found using the calculation program (see also Annex 3)

Where an explosion occurs in a room, the differences between the maximum pressures that can be obtained if the room remains intact are irrelevant as the room will break down at internal overpressures of a much lower level.

12.7 Exposure to Toxic Vapours in a Room

As for asphyxiation, the minimum release that gives rise to toxic effects can be determined. Figure 12.3 shows the relationship between the exposure time and the concentration of ammonia as a function of the probability of death [64]. This relationship depends on the lethality data used - in this case the most conservative[1].

Figure 12.3 Effects of exposure to ammonia vapour



If 2000 mg/m^3 is taken as a dangerous concentration of ammonia (a 1% chance of death after exposure for 30 minutes) it is possible to determine the required release in a room (or release rate in the case of a continuous release) to obtain this concentration.

For an instantaneous release the maximum concentration is found at the time of the release as shown in the following equation:

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[1] With respect to the toxicity, other data are to be found in Reference [68]

$$C_{max} = \frac{M}{pV} \text{ x } 100\% \tag{12.1}$$

In the case of ammonia, the concentration of 2000 mg/m^3 and the density of the vapour are known, so the minimum dangerous release can be defined as where:

$$M > 2 \text{ x } 10^{-3} \text{ V} \tag{12.2}$$

where:
M = released mass (kg)
V = volume of chamber (m^3)

The same approach is possible for a continuous release. If no ventilation is assumed, the maximum concentration is given using the following equation:

$$C = \frac{m}{pV} \text{ x t x } 100\% \tag{12.3}$$

where:
m = mass release rate (kg/s)
t = time since release (s)
V = volume of chamber (m^3)

The concentration in the room will theoretically increase until a pure ammonia atmosphere is reached. Using Formula 12.3 for a concentration of 2000 mg/m^3 reached after 10 minutes, the minimum release is give by:

$$m > 3.4 \text{ x } 10^{-6} \text{ V} \tag{12.4}$$

This rule of thumb can easily be applied for other fluids as well as for other concentrations of interest.

12.8 Dispersion of Toxic Vapours

A generalised method is used here [68] to determine the effects of toxic vapours dispersed in the environment. A distinction is made between:

- an instantaneous release of a liquefied gas;
- a continuous gas release.

Fundamental to this method is a classification which is based on the toxicity of the fluid and the total fluid content in the installation (instantaneous release) or the diameter of the release opening (continuous release).

Points are ascribed to the toxic fluid as a function of the LC_{50} value (in ppm, for rats, and for an exposure time of four hours):

LC_{50} value	**No of points**
0.01 - 0.1	8
0.1 - 1	7
1 - 10	6
10 - 100	5
100 - 1000	4
1000 - 10,000	3
> 10,000	2

Additional points are given for the release of a liquefied toxic fluid on the basis of its boiling point (see below). In the case of a gas release, additional points are given as a function of the release pressure (see below).

Instantaneous release
To determine the area of impact for the release of a liquefied toxic gas, additional points have first to be given as a function of its atmospheric boiling point:

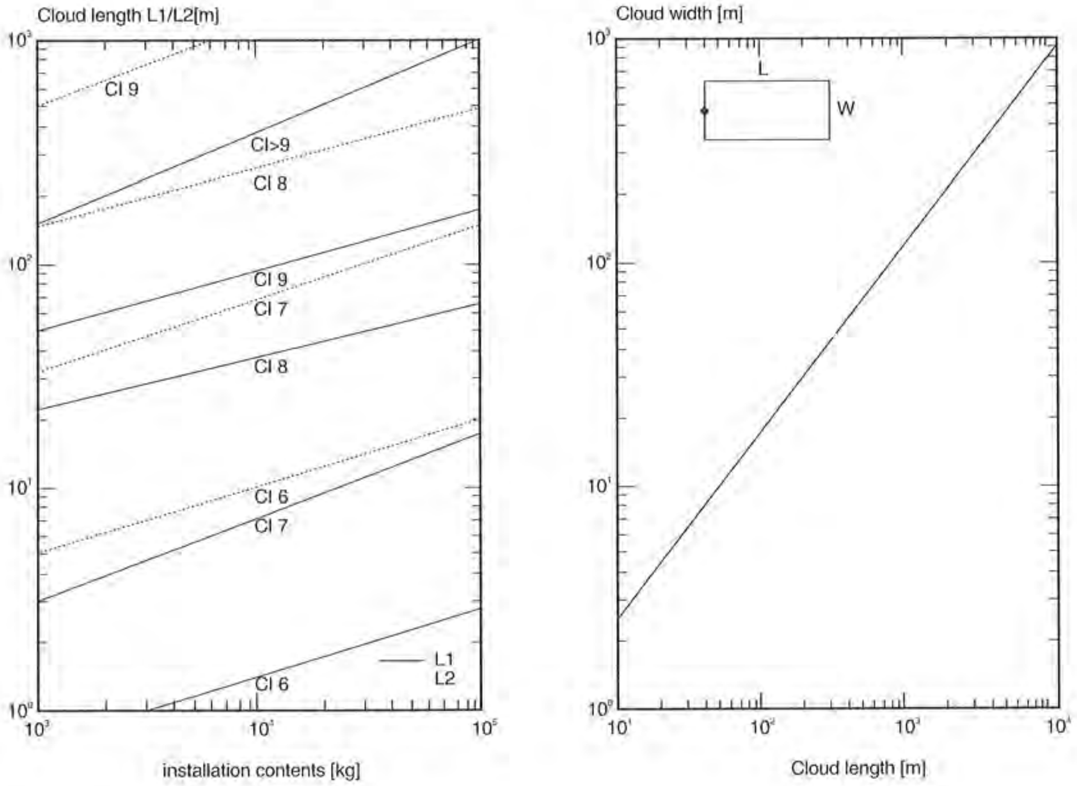
- a boiling point > -10°C receives 3 points;
- a boiling point < -10°C receives 4 points.

The class of the toxic fluid is then found by adding the points given on the basis of boiling point and toxicity. In the case of ammonia, where the boiling point is < -10°C and the LC_{50} is 1000 - 10,000 ppm, the class can be found by adding, respectively 4 and 3, giving 7 points.

In Figure 12.4 the relevant distances, L1 and L2, can be found from the total content of the installation and the classification as described above. L1 and L2 determine the length of the cloud within which, respectively, death and injury (reversible) can be expected if people are exposed for a period of at least 30 minutes.

The right-hand of the two graphs enables the width of the cloud to be determined once the length is known.

Figure 12.4 Impact area for the release of liquefied toxic gases



Continuous gas release

To determine the area of impact for the continuous release of a toxic gas, additional points must first be given as a function of the release pressure:

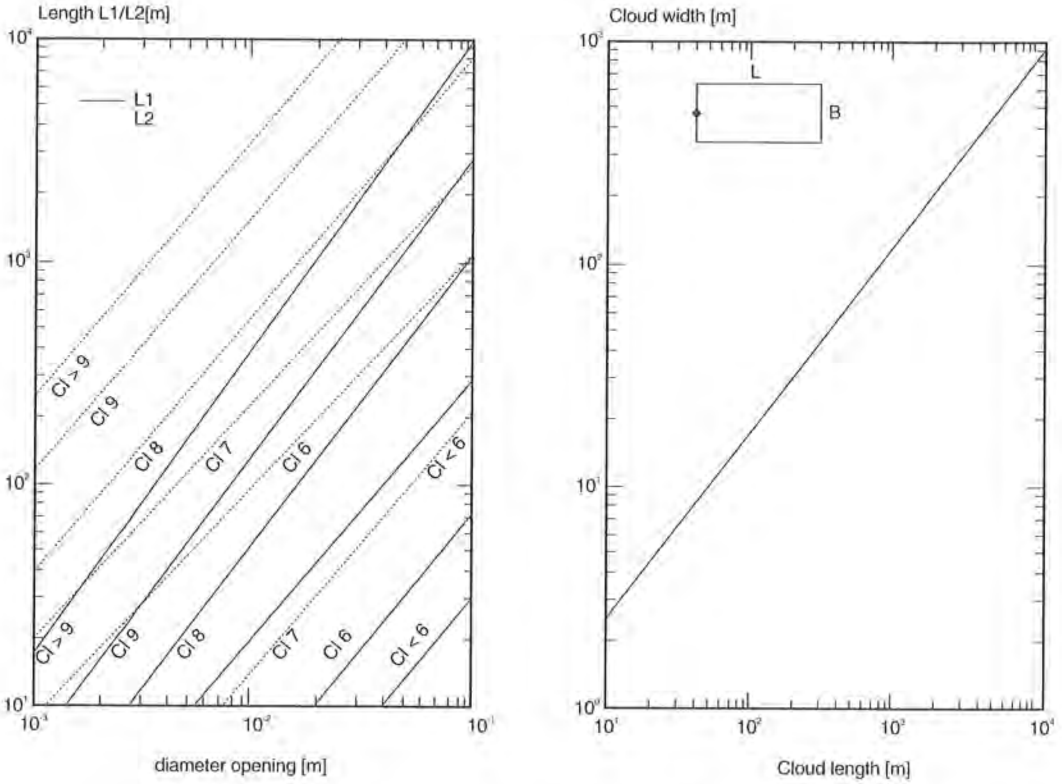
- a release pressure of < 3 bar receives 2 points;
- a release pressure of 3-25 bar receives 3 points;
- a release pressure of > 25 bar receives 4 points.

The class of the toxic fluid is then found by adding the points given on the basis of release pressure and toxicity. For ammonia with an assumed release pressure of 10 bar and an LC_{50} value of 1000 - 10,000 ppm, the class can be found by adding, respectively, 3 and 3, giving 6 points.

In Figure 12.5 the relevant distances, L1 and L2, can be found from the diameter of the opening and the classification. L1 and L2 determine the length of the cloud within which, respectively, death and injury (reversible) can be expected if people are exposed for a period of at least 30 minutes.

The right-hand of the two graphs enables the width of the cloud to be determined once the length is known.

Figure 12.5 Impact area for the release of toxic gases



An estimate of the impact area with respect to the toxic effects of the released fluids is thus easily found.

12.9 Toxic Flue Gases

Toxic flue gases can be formed when toxic, flammable fluids are produced in a fire. As already discussed (Section 10.2), the effects of toxic flue gases are to be expected only within a room or a building. Because the toxic concentration is far below the flammability limit, toxic effects from exposure to the fluid vapours will occur first.

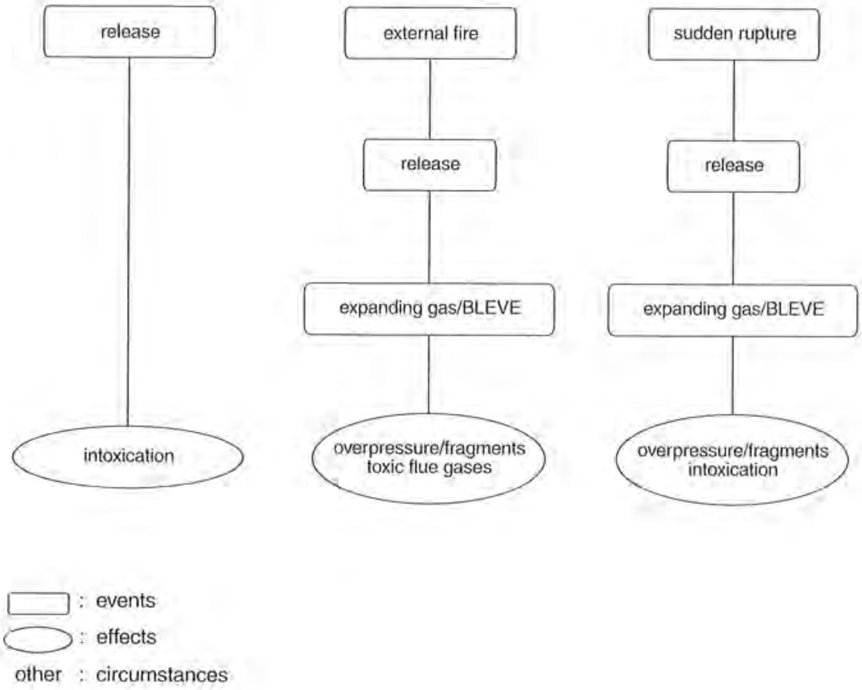
In the case of large fires, the flammability of the working fluid will enhance both the fire and the dispersion of the flue gases within the environment. Only at the start of a fire, when the plume rise is limited, may toxic concentrations be found in the immediate surroundings of the fire. Specific circumstances will be very important in this case, so an estimate of relevant distances is very difficult. The effects of smoke and heat radiation will also be present, tending to keep people away from the fire.

13. THE EFFECTS OF ACCIDENTS INVOLVING A TOXIC, NON-FLAMMABLE WORKING FLUID

Figure 13.1 gives an overview of the scenarios and effects associated with accidents involving a toxic, non-flammable working fluid. The only hazards are those relating to intoxication and the effects of overpressure and fragments. The number of working fluids in this category is limited. Sulphur dioxide (R764) will be taken as representative of this type of working fluid. Another typical example is dichloromethane (R30) which burns only under specific circumstances, for example an oxygen-enriched atmosphere.

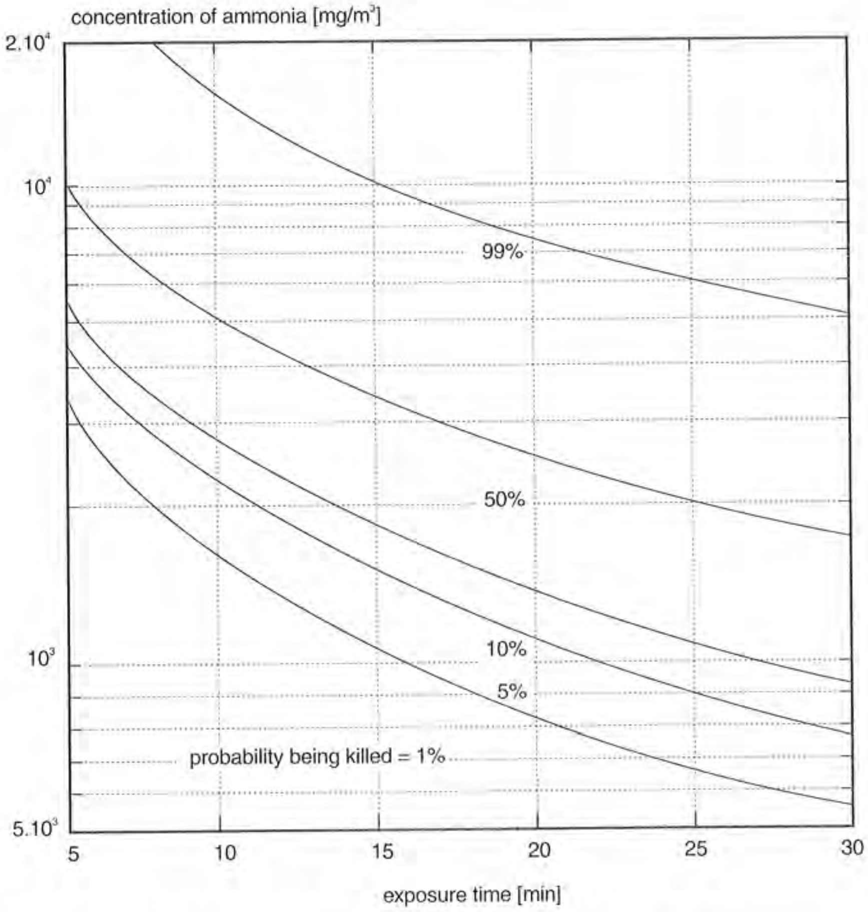
If the effects shown in Figure 13.1 are compared with those for the group of non-toxic, non-flammable working fluids (Figure 10.1), the only difference is that exposure to the working fluid vapour will give rise to intoxication rather than asphyxiation. This means that, for all effects with the exception of intoxication, reference can be made to Sections 10.2-10.4.

Figure 13.1 Overview of scenarios and effects associated with an accident involving a toxic, non-flammable working fluid



For exposure to toxic vapours in a room, reference is made to Section 12.7. Figure 13.2 shows the effects of exposure to sulphur dioxide vapour. A reference concentration of 600 mg/m^3 is used in this case (a 1% chance of death after an exposure of 30 minutes).

Figure 13.2 Effects of exposure to sulphur dioxide vapour



For the dispersion of toxic vapours, reference is made to Section 2.8. Because the LC_{50} value (for rats after a four-hour exposure) is between 1000 and 10,000 ppm, the same classification holds for sulphur dioxide as for ammonia with respect to the areas of impact.

14. CONCLUSIONS

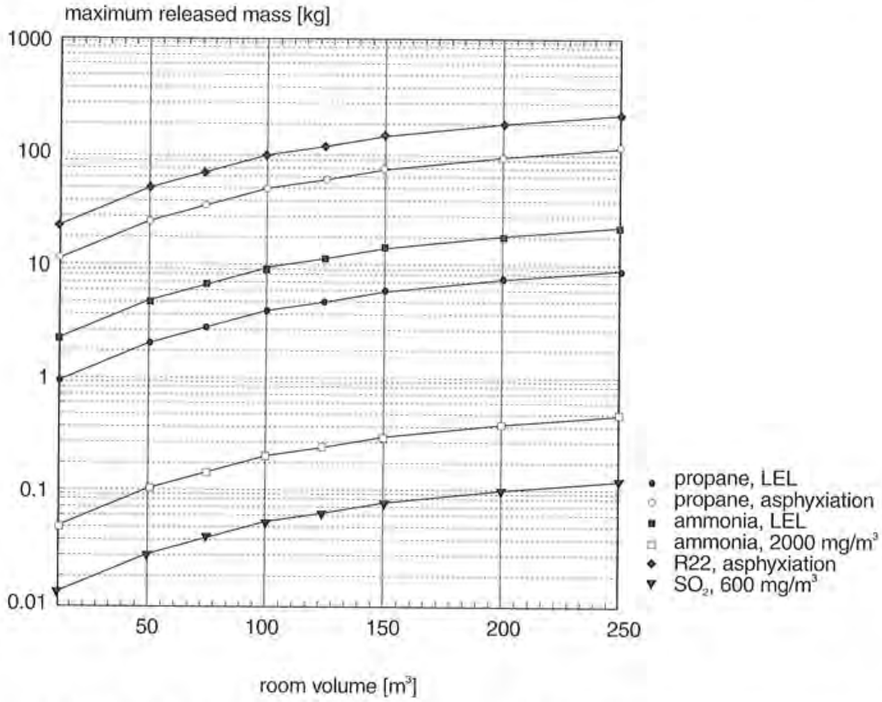
Part Two of this report confirms that the expected effects arising from accidents with working fluids are related mainly to their flammability and toxicity.

Accidents with non-toxic, non-flammable working fluids result in the minimum range of possible effects. These effects (asphyxiation, overpressure/fragments from a vessel rupture, toxic flue gases) are also characteristic of other types of working fluid. However, a working fluid that is flammable and/or toxic is more dangerous.

With respect to flammability, the difference between the typical flammable working fluids and those which are both toxic and flammable is discussed in Section 12. This shows that, for typical toxic, flammable working fluids, the hazards of fire and explosion are less than for those working fluids that are flammable only. When flammability alone is taken into account, the toxic, flammable working fluids are to be preferred over the flammable working fluids.

With respect to toxicity, Figure 14.1 shows the amount of each fluid needed to generate a dangerous situation in the case of an instantaneous release.

Figure 14.1 Maximum mass of working fluid that will generate a dangerous situation in the case of an instantaneous release in a room



From this figure it is clear that toxic effects can be expected for a released mass that is one or two orders of magnitude smaller than the concentration of a flammable working fluid with possible fire and explosion effects.

Figure 14.1 is also valid for a continuous release as it gives the total released mass required to generate a dangerous concentration at the end of the release period if there is no ventilation. If ventilation does occur, the released masses are higher, but the same relationship between the various working fluids will remain.

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ANNEX 1
REFRIGERATION STANDARDS

This comparison of national and international standards dealing with the safety requirements of mechanical refrigeration systems is based on the standards listed in Table A1.1

Table A1.1 National and international standards examined

Country		**Documentation**
United Kingdom	BS 4434	British standard, British Standards Institution, UK (BSI)
Belgium	NBN E35-001	Belgian standard, Belgisch Instituut voor Normalisatie, Belgium (NBN)
Netherlands	NEN 3380	Dutch standard, Nederlands Normalisatie Instituut, The Netherlands (NEN) '*Eisen behorende bij het besluit ozon aantastende stoffen*', TNO, The Netherlands (TNO)
Switzerland	SN 25130	Swiss standard, Societe Suisse des Constructeurs de Machines, Switzerland (SN)
USA	ASHRAE 15-1989-R	American standard, American Society of Heating, Refrigeration and Air-Conditioning Engineers, US (ASHRAE)
Japan		'*Japanese Regulations on Refrigerants*', Japan (JR)
	KHKS 0402	Facility standard for Refrigeration Units, High Pressure Gas Safety Institute, Japan (KHK)
	MITI Ordonance	High Pressure Gas Control Law, Japan (MITI) '*Supplementary Standard for Refrigeration Safety Regulations*', Japan (SSRSR)
Germany	DIN 8975	German standard, Deutsches Institut fur Normung, Germany (DIN)
Sweden	Svesk Kylnorm	Swedish standard, Kylbranchens Samarbetsstifelse, Sweden (SK)
Norway	Norsk Kuldenorm	Norwegian standard, Samarbeidsutvalget for Kuldebransjen, Norway (NK)
France	NF E35-400	French standard, Association Francaise de Normalisation, France (NF)
International	ISO-DIS-5149	International standard, International Organisation for Standardisation (ISO)

In order to make a comparison possible, the standards will be discussed under ten headings, each dealing with a specific topic:

- A1.1 Specific Dangers and Scope
- A1.2 Refrigerant - System - Occupancy Classification
- A1.3 Pressure (Design - Protection - Testing)
- A1.4 Machinery Rooms
- A1.5 Alarm and Detection
- A1.6 Electrical Installation
- A1.7 Instrumentation
- A1.8 Materials - Piping - Fittings
- A1.9 Marking - Certification - Instruction - Maintenance
- A1.10 Miscellaneous Special Requirements

Table A1.2 details the section numbers for each standard that are discussed under the various headings. In this way, the reader can easily compare the exact formulations of the regulations in different standards.

Table A1.2 Overview of the relevant section numbers for each standard

	BSI	NBN	NEN	SN	ASHRAE	ISO	JN	DIN	SK	NK	NF
Specific dangers and scope	Introduction & 2.21	Inleiding & 1.3	Inleiding	/	/	Foreword & 2.28	-	1-10:1	9	2.1.3.	1.2
Refrigerant classification	3.1	2.3	9	5	6	3.3	JN: Refrigerant classification	Teil 1: Tabelle 1	3.2	3.2	3.3
System classification	3.1	2.2	8	4	5	3.2	KHK 3.2.1, 3.5.2, 3.19.6	/	3.1	3.1	3.2
Occupancy classification	1	2.1	7	3	4	5.3	JN: Equipment standards	/	3.3	3.4	3.1
Maximum charge of refrigerants	3.2	6.2.1-6.2.4	9&60-65	7	7	5.3	-	/	7.2-7.4	4.2-	5
Pressure design, protection, testing	3.3, 3.7, 5.1-5.4 4.1.6	3.1, 3.3, 3.5, 5.1-5.5	10-15, 23-28, 36-43, 16	/	8-10	4.1, 4.3, 4.7	MITI: Chapter 4	1, 4.3, 5, 6.4, 7, 10.3.2.2	5.2, 6.1, 7.9, 10.6, 10.7	6.3, 6.5, 1.2, 6.6, 7.8, 7.9, 11	4.1, 4.5
Machinery room	4.2	6.1	59-59	6, 7.1.2, 7.2.2, 7.3	11.13, 11.14	5.1, 5.3, 2.2, 15.3.3	KHK: 3.2.1, 3.5.2, 3.19.6	/	8	4.2.2.2.1 4.2.3.2.1 4.2.4.2.1 4.2.5	4.7
Alarm and detection	4.3.2, 4.4, app.F-2	4.2.2.2.6 4.2.3	45.3, 46	7.2.1.3 6.4	11.13, 11.14	4.8.3, 4.8.2.3	KHK:12	/	8.4-8.6, 8.9, 11.2	4.2.5.3.2	4.6.2, 3.3.4.2
Electrical installation	4.5	4.2	44-46, 58.g-h	6.2.f-g	11.13, 11.14	4.8	KHK:6	/	8.7-8.9, 8.11, 12.4.3	4.2.5.3.3	4.6
Instrumentation	3.8	3.4	33-35	/	/	4.6	-	6.10, 8	5.8-5.10	6.5.1.1, 6.6.8.2, 6.6.8.3, 6.6.9.1	4.4
Materials, piping, fittings	3.6, 4.1.3, 5.5, app. B&C	3.2, 4.1, 6.2.2.2.2 6.2.3.2.3	17-22, 29-30, 62.2, 64.2	7.1.3, 7.2.3, 7.3	8.1, 8.4, 9.3, 10.4.8, 11.12	4.2, 4.4, 5.3.1.2.2 5.3.2.2.2	SSRSR: 16.1	2, 6, 9, 10.2.3.6 10.2.3.8	4, 5.3, 5.5, 7.6	7.3 7.4-7.10	A.2.3, 4.3 5.1.2.2, 5.2.2.3, 5.3
Marking, certification, instruction maintenance	6, 7	3.3.3, 7.1.1, 7.1.2	16, 25-27, 68-72	/	8.8, 12, 13 & KHK 16	4.3.3-4.3.4, 5.2.7, 6.1	MITI: 45, 45.2, 46 10.7-10.9	3, 4	6, 8.10, 9.4,	4.2.5.3.4.5, 6.5.1, 6.6.5, 6.7.1, 6.8.1, 6.9, 6.10, 7.7, 10	6
Miscellaneous special requirements	4.1, 4.2, 4.6, part 2	4.3, 7.1, 7.2	46-56, 70-72, 73-77	6.1, 7.1.2.1	13.9, 13.7	5.2, 6, annex B	JN: High pressure gases RSR: 11 KHK: 9.1.1, 12 and SSRSR: 12	3.12.5, 4.4.3, 6.5, 10.32.3., 10.4.3.1, 10.4.4, ...	11, 12, 13, 14	4.4, 4.5, 4.6	4.8, 7.2, 7.3

/ = Item is not in this standard - = Regulation was insufficiently known (because only an English summary of a Japanese text was ayaillable)

A1.1 Specific Dangers and Scope

A1.1.1 Specific dangers

Only the BSI, NBN and ISO standards mention the specific dangers involved with the use of refrigeration systems.

A1.1.2 Scope

Most of the standards are applicable to both large and small refrigeration systems (SN, ASHRAE and Japanese regulations do not mention scope). Only BSI, NBN, NEN, ISO, SK and NK define the difference between large and small systems. The French standard NF is only applicable to large systems. Table A1.3 gives a classification of small systems as a function of their maximum refrigerant charge. In Japan, a classification is made according to nominal refrigeration capacity.

Table A1.3 Classification of small systems (maximum refrigerant charge)

Refrigerant class	BSI	NBN	NEN	ISO	SK	NK	NF
Group 1	10 kg	10 kg	5 kg	10 kg	3 kg	3 kg	25 kg
Group 2	2.5 kg	2.5 kg	2.5 kg	2.5 kg	0.5 kg	0.5 kg	2.5 kg
Group 3	1 kg	1 kg	0 kg	0 kg	0.5 kg	0.5 kg	0 kg

A1.2 Refrigerant - System - Occupancy Classification

A1.2.1 Refrigerant classification

BSI, NBN, NEN, SN, ISO, DIN, SK, NK and NF apply the following refrigerant classification:

- Group 1: non-toxic, non-explosive refrigerants;
- Group 2: mainly toxic refrigerants (LEL > 3.5%, highly toxic at this concentration);
- Group 3: mainly explosive refrigerants (LEL < 3.5%, non-toxic at this concentration).

NBN, the Dutch TNO document and NK use a subgroup of Group 1 to classify the 'hard CFCs', i.e. the ozone-depleting CFCs (R11, R12, R113, R114, R115 etc). DIN and SK mention these refrigerants as being harmful to the environment without putting them in a subgroup.

ASHRAE uses a completely different, six-group classification based on toxicity and flammability:

- Group A: almost non-toxic refrigerants (TLV value > 400 ppm)
  - A1: non-explosive refrigerants
  - A2: explosive (LEL > 0.1 kg/m^3 and a heat development < 19 kJ/kg)
  - A3: very explosive (LEL < 0.1 kg/m^3 or a heat development > 19 kJ/kg)
- Group B: toxic refrigerants (TLV value < 400 ppm)
  - B1: non-explosive refrigerants
  - B2: explosive (LEL > 0.1 kg/m^3 and a heat development < 19 kJ/kg)
  - B3: very explosive (LEL < 0.1 kg/m^3 or a heat development > 19 kJ/kg)

These equate, approximately, to the following:

- Group 1 (BSI and others) ≈ Group A1 (ASHRAE)
- Group 2 (BSI and others) ≈ Groups A2, B1 and B2 (ASHRAE)
- Group 3 (BSI and others) ≈ Groups A3 and B3 (ASHRAE)

The Japanese regulations use three different refrigerant groups:

- Group 1: non-toxic and non-flammable refrigerants. This group is subdivided into three subgroups according to the evaporation pressure at 35°C.
- Group 2: toxic and/or flammable refrigerants.
- Group 3: very toxic and/or very flammable refrigerants.

The standards BSI, NBN, NEN, ASHRAE, ISO, SK, NK and NF contain tables with maximum allowable concentrations, although values for Groups 2 and 3 are absent in SK. In SN, reference is made to another document (SN 253120). In DIN, tables with concentrations are completely lacking.
The Dutch TNO document, NK and ASHRAE are the only ones which discuss new refrigerants such as R134a and R123.

Apart from BSI, the European maximum concentrations do not differ substantially.
ISO and BSI concentrations are almost as stringent as the European ones, but ASHRAE concentrations are 2.5-3.0 times smaller.

A1.2.2 System classification

BSI, NBN, NEN, SN, ISO, the Japanese Regulations, SK and NF agree completely on refrigeration system classification. They mention direct systems, indirect open systems, indirect vented open systems, indirect closed systems, indirect vented closed systems and double indirect systems. In ASHRAE, the indirect vented open system is absent. NK only mentions the difference direct-indirect, but never uses it. In DIN, a system classification is never used.

A1.2 3 Occupancy classification

BSI, NEN, SN, ASHRAE, ISO, NK and NF have five occupancy room groups (A-E).
NBN is different:

- A, B and C (BSI and others) ≈ A (NBN)
- D (BSI and others) ≈ B (NBN)
- E (BSI and others) ≈ C (NBN)

TNO and SK:

- A and C (BSI and others) ≈ A (TNO and SK)
- B and D (BSI and others) ≈ B (TNO and SK)
- E (BSI and others) ≈ C (TNO and SK)

The Japanese regulations:

- A (BSI and others) ≈ A (Japanese)
- B and C (BSI and others) ≈ B (Japanese)
- D (BSI and others) ≈ C and D (Japanese)
- E (BSI and others) ≈ E (Japanese)

DIN makes no use of an occupancy room classification.

A1.2.4 Maximum charge of refrigerant: use of cooling and heating system

This section uses the British refrigerant, refrigeration system and occupancy room classification. As far as is possible, the other standards are related to this classification.

Group 1

The same regulation is valid in BSI, NBN, NEN, SN, ISO and NF: the refrigerant charge must not exceed the value c x V, where c is the maximum allowable concentration and V the total space volume (including the volume of all ventilated spaces if the air circulation capacity cannot be reduced below 25% of its maximum). If the refrigeration systems are installed in the open air or in a machinery room, there are no restrictions (unless a direct or an indirect open system is used). They can also be used freely in rooms of Group E. In SN, there is no table of maximum concentrations.

The ASHRAE standard and the Swedish standard make a further distinction with respect to the occupancy room, the ASHRAE standard being by far the most restrictive as its maximum concentrations are 2.5-3.0 times lower than those for the other standards.

The Japanese standard is completely different. It does not make use of any maximum concentration.
NK makes no distinction between direct and indirect systems.

In DIN, there are no requirements relating to refrigerant charge.

Group 2

Group 2 regulations are by far the most difficult to compare.
Only NEN, ASHRAE and NF make use of maximum concentrations.
In SN, there are some special requirements for 'small systems'. Nowhere, however, are they defined.
NK makes no distinction between direct and indirect systems.
In DIN, there are no requirements relating to refrigerant charge.

Group 3

NBN, NEN, SN and ISO are in agreement:

- Type A, B and C: Group 3 refrigerants not allowed
- Type D:Only in laboratories, max. refrigerant charge 2.5 kg
- Type E: Special explosion safety precautions should be taken

BSI has the same regulation, except for Type E. This sets a 2.5 kg maximum refrigerant charge in rooms where occupancy is more than one person per 10 m^2. There are no restrictions, however, if the system is installed in a machinery room.

ASHRAE has the same regulation for A, B and C as NBN and others. For Type D, the maximum refrigerant charge is 3 kg in rooms where occupancy is more than one person per 10 m^2. For Type E, the refrigerants in this group are not to be used for air conditioning, except for indirectly vented systems. Special precautions are also needed.

Japanese regulations have the same regulation for A, B and C as NBN and others. Type D: where Group 3 refrigerants are used for air conditioning, they may only be used, with some exceptions, for small absorption systems. In other applications, a 70 kW maximum is imposed. Type E: unlimited use.

NK has the same regulation for A, B and C as NBN and others. Type D: only in laboratories. Types D and E: special permission must be obtained from the local fire brigade.

The Swedish standard forbids the use of Group 3 refrigerants in Type A, B, C and D rooms. In the case of Type E, special permissions must be obtained from the local fire brigade. However, unit systems with a total charge of 1.5 kg may be installed in laboratories, irrespective of room category.

In NF, the use of Group 3 refrigerants is not allowed in Type A, B, C and D rooms. In the case of Type E rooms, special explosion safety precautions must be taken.

A1.2.5 Overview: refrigerant classification

Table A1.4 identifies the number of groups according to the different classifications

Table A1.4 Classification of refrigerant groups

	BSI	NBN	NEN	SN	ASHRAE	ISO	JN	DIN	SK	NK	NF
Number of refrigerant groups	3	3	3	3	6	3	5	3	3	3	3
Number of system groups	6	6	6	6	5	6	6	0	6	0	6
Number of occupancy room groups	5	3	5	5	5	5	5	0	3	5	5

A1.3 Pressure (Design - Protection - Testing)

SN regulations on pressure (design - protection - testing) are completely lacking.

Although the ASHRAE standard is quite elaborate regarding design pressure and protection against excessive pressure, it is inconveniently arranged. For instance, no distinction is made between design pressure and maximum working pressure, and paragraphs about pressure vessels are mixed with paragraphs about testing.

A1.3.1 Design

Definitions of maximum working pressure and design pressure are almost the same for BSI, NBN, NEN, ISO, SK, NK and NF. In ASHRAE and DIN, no definition of maximum working pressure is given. All of these standards refer to a pressure vessel standard (Table A1.5).

Table A1.5 Pressure vessel standards

	BSI	NBN	NEN	SN	ASHRAE	ISO	JN	DIN	SK	NK	NF
Pressure vessel standard	BS 5500	BS 5500	Grond slagen..'	/	ASME Boiler and Pressure Vessel Code	National or international codes	MITI	TRB	AFS 1986:9 & TKN	TBKI	Reglementation des Appareils a Pression

Key

/ Item is not treated in this standard

A1.3.2 Protection

BSI and ISO define 'intrinsically pressure safe' refrigeration systems as those systems in which the pressure will not exceed the maximum working pressure during operation or at rest, because of either the internal construction of the motor compressor or the volume of the refrigerant-containing parts in relation to the mass of refrigerant. These systems do not need special protection. DIN's intrinsically safe systems do, however, need either a pressure discharge device discharging to the low pressure side or a fusible plug.

All of the standards require large systems to be protected against excessive pressure. Protection is also required for pressure vessels of a certain volume which may contain liquid refrigerant and which may be shut off from other parts of the refrigerating system. Positive displacement compressors and pumps, with some exceptions (see standard), also need to be protected. Non-positive displacement compressors need only be protected if excessive pressure can occur.

A1.3.3 Testing

All components must be tested.

Strength test

BSI, NBN, NEN, ISO, SK, NK and JN	For castings: at least 1.5 times the component design pressure For rolled or drawn components, at least 1.3 times the component design pressure
ASHRAE, DIN, NF	No regulations on strength tests

Leakage test

BSI and NK	At 1.1 times the design pressure
NBN and NEN	At the maximum working pressure (but not less than 2 bar)
ISO, DIN and JN	At the design pressure
ASHRAE, SK, NF	No regulations on leakage tests

Repeat strength test

Only BSI, NBN, NEN, ISO and DIN discuss repeat strength tests.

A1.4 Machinery Rooms

DIN has no regulation on machinery rooms.

Dimensions and access

SK is by far the most elaborate on dimensions and access. It includes regulations about mounting in a pit, machinery room doors, fire escapes etc.

Ventilation

NBN, NEN, SN, ASHRAE, JN and NF give a formula for calculating the air circulation capacity as a function of the total refrigerant charge. ASHRAE is more restrictive than the others. SK uses the same formula for mechanical ventilation but does not allow natural ventilation, even as basic ventilation (two air changes per hour). NK imposes two air changes per hour, which can be reduced to one air change per hour if a Group 1 refrigerant is used.

Water sprinklers

Only NBN, NEN, ISO, JN and NK recommend water sprinkler devices when using ammonia refrigeration systems.

Special precautions

BSI, NBN, NEN, SN, ASHRAE, ISO and NF contain a list of special precautions that have to be taken if the machinery room has to be isolated from the rest of the building. NBN, NEN, SN and ISO prescribe special precautions according to the group of the refrigerant used in the machinery room. They have the most elaborate regulations on explosion safety.

A1.5 Alarm and Detection

A1.5.1 General

DIN does not consider alarm and detection.

In Japan, safety devices are mandatory for refrigeration equipment of more than 20 rT nominal refrigeration capacity.

NEN, SN and NF prescribe detectors only for ammonia.

BSI, ASHRAE and ISO do not consider detectors in occupancy rooms.

A1.5.2 Detailed analysis

Different refrigerant groups require different alarm and detection regulations. A distinction is made in the BSI classification between:

- Group 1;
- Group 2;
- Group 3;
- Ammonia as a special case from Group 2.

Group 1

BSI	Alarm and emergency ventilation shall be activated if the maximum concentration is exceeded.
NBN	Applies only if the refrigerant charge is > 500 kg. Alarm shall be activated if the maximum concentration is exceeded.
NEN, SN, ISO, NF	No detectors required.
ASHRAE	An oxygen sensor gives an alarm if the oxygen concentration falls below 19.5%.
SK	Applies only if refrigerant charge is > 1000 kg. Detection takes place at two levels: a low-level alarm for a concentration corresponding to the hygienic limit and a high level alarm at dangerous concentrations. An oxygen deficiency alarm should be activated below the 20% oxygen level.
NK	Applies only if the refrigerant charge is > 1000 kg or if the system is installed underground. Alarm shall be activated if the TLV value is exceeded (or if an oxygen deficiency of less than 20% oxygen is detected).
JN	The types and number of safety devices are defined.

Group 2

BSI	Alarm and emergency ventilation shall be activated if the concentration exceeds 1%.
NBN	Applies only if the refrigerant charge is > 500 kg. Alarm shall be activated if the maximum allowable concentration is exceeded.
NEN, SN, NF	No detectors required.
ASHRAE	Alarm shall be activated if the TLV value is exceeded.
ISO	Alarm shall be activated if a concentration of 25% of the LEL value is exceeded.
SK	Operating circuit for refrigeration system is switched off, alarm and mechanical ventilation are activated if a certain concentration is exceeded. An oxygen deficiency alarm should be activated below a minimum oxygen level of 20% (only if refrigerant charge is > 1000 kg).
NK	Alarm shall be activated if the TLV value is exceeded.
JN	The types and number of safety devices are defined more strictly than for Group 1.

Group 3

BSI	Alarm and emergency ventilation shall be activated if the concentration exceeds 30% of the LEL.
NBN, ISO	Alarm shall be activated if the concentration exceeds 25% of the LEL.
NEN, SN, NF	No detectors required.
ASHRAE	Alarm shall be activated if the TLV value is exceeded.
SK	Alarm and emergency ventilation shall be activated if the concentration exceeds a certain value related to the LEL value (see standard).
NK	Alarm shall be activated if the LEL value is exceeded.
JN	A description identical to that for Group 2 is made.

Ammonia

BSI	10,000 ppm	Alarm and emergency ventilation shall be activated.
NBN	200 ppm	(500 ppm in machinery room). Alarm and mechanical ventilation are activated.
	10,000 ppm	Operating circuit for refrigeration system is switched off.

NEN	10,000 ppm	Operating circuit for refrigeration system is switched off: alarm and mechanical ventilation are activated.
SN	200 ppm	Alarm and mechanical ventilation are activated.
ASHRAE, ISO	40,000 ppm	Alarm and mechanical ventilation are activated.
SK	? ppm	Operating circuit for refrigeration system is switched off: alarm and mechanical ventilation are activated. If ammonia charge is > 1000 kg, an oxygen deficiency alarm shall be activated below a minimum oxygen level of 20%.
NK	500 ppm	Applies only if ammonia charge is > 1000 kg. Alarm is activated.
	10,000 ppm	Mechanical ventilation is activated, operating circuit for refrigeration system is switched off etc.
NF	2000 ppm	Operating circuit for refrigeration system is switched off: alarm and mechanical ventilation are activated.
JN	?	

A1.6 Electrical Installation

DIN does not discuss electrical installation.
SN, ASHRAE and NK do not discuss electrical installation in a special chapter. Rules are difficult to find.

Independent circuits

Independent circuits must be provided for:
- the refrigeration system power supply (all standards);
- the alarm (BSI, NBN, NEN, ISO, SK, NK, JN and NF);
- lighting (only JN and NF).

Switches

In NBN, NEN, SN, ISO, JN and SK, switches for mechanical (emergency) ventilation shall be provided both inside and outside the refrigeration machinery room. In BSI, switches outside the machinery room suffice.

Hazardous areas

Refrigeration systems working with flammable refrigerants shall be provided according to the requirements for hazardous areas (Table A1.6) (all standards).

Table A1.6 Explosion safety standards

	BSI	NBN	NEN	SN	ASHRAE	ISO	JN	DIN	SK	NK	NF
Explosion safety requirements	BS 5345 and 4683	AREI (EXe)	NEN 1010	CNA and ASE	ANSI/NFPA 70-1990	/	/	/	AFS 1985:17	/	BE3

Key
/ Item is not treated in this standard

Condensation
Special precautions must be taken if condensation can occur (BSI, NBN, NEN, ISO, SK and NF).

A1.7 Instrumentation
In SN and ASHRAE, regulations on instrumentation are completely lacking.

A1.7.1 Pressure gauges
Compressors shall be equipped with pressure gauges if the charge mass of the system exceeds the limits given in Table A1.7.

Table A1.7 Maximum refrigerant charge for which no pressure gauge is required

Refrigerant class	BSI	NBN	NEN	ISO	DIN	SK	NK	NF
Group 1	50 kg	100 kg	50 kg	100 kg	100 kg	/	/	25 kg
Group 2	25 kg	25 kg	25 kg	25 kg	0 kg	/	/	2.5 kg
Group 3	0 kg	1 kg	0 kg	1 kg	0 kg	/	/	0 kg

NF does not discuss so-called 'small systems'. Installations operating with refrigerants of Groups 1 or 2 and with a compressor consuming 10 kW or less only need to be equipped with a pressure gauge connection.

In DIN, installations operating with less than 100 kg of Group 1 refrigerant only need to be equipped with a pressure gauge connection.

In ISO, for systems containing more than 10 kg of Group 1 refrigerant or more than 2.5 kg of Group 2 refrigerant, pressure gauge connections shall be provided (the fitting of permanent pressure gauges being optional). Gauges or gauge connections may be omitted in systems containing up to a mass of 10 kg of Group 1, 2.5 kg of Group 2 or 1 kg of Group 3 refrigerant.

In ISO, pressure vessels containing more than 100 l, which may contain liquid refrigerant and which may be shut off from other parts of the refrigeration system, shall also be provided with a pressure gauge.

In Japan, no provisions are made for equipment below 3 rT of nominal refrigeration capacity. For ammonia the use of special pressure gauges is mandatory.

A1.7.2 Liquid level indicators

Glass tube liquid level indicators shall be guarded against wanton or accidental damage to prevent injury to observers in the event of glass breakage (BSI, NBN, NEN, ASHRAE, ISO, JN and NF).
DIN is very elaborate concerning liquid level indicators.

Placement of liquid level indicators is also recommended on pressure vessels which may contain liquid refrigerant, have a diameter greater than 300 mm and a content greater than 30 l (NBN) or 50 l (NEN).

In ISO, refrigerant receivers in systems containing more than 10 kg of Group 1 refrigerant, 2.5 kg of Group 2 refrigerant or 1 kg of Group 3 refrigerant, and which may be isolated, shall be provided with a liquid level indicator.

In NK, evaporators, condensers and pressure vessels with a capacity greater than 300 l shall be provided with a liquid level indicator.

BSI, SN, ASHRAE, ISO, DIN, SK and NF do not discuss the arrangement of liquid level indicators.

A1.8 Materials - Piping - Fittings

A1.8.1 Materials

When choosing materials, consideration should be given to mechanical strength, chemical compatibility and reaction to thermal influences. In particular, they have to be compatible with the refrigerant and the lubricant (BSI, NBN, NEN, ASHRAE, ISO, DIN, SK, JN and NK).

A1.8.2 Piping and fittings

Fittings by brazing and welding are discussed in BSI, NBN, NEN, ASHRAE, ISO, DIN, SK and NK. NF and JN refer to the 'Arrete Ministeriel du 24 mars 1978'.

ASHRAE, DIN, SK and NK extensively describe all kinds of fittings.

All standards discuss the arrangement of piping, often as a function of the refrigerant group.

A1.8.3 Location of refrigerant piping

The location of piping is discussed for the different groups of refrigerant.

Group 1

BSI, NBN, NEN,	In occupancy rooms of Categories A, B and C, piping shall be laid in
SN, ISO, NF	fire-resistant ducts vented to the atmosphere (NBN, NEN and NF), or eventually to the machinery room (BSI, SN, ISO).
ASHRAE, DIN, SK, NK	No restrictions

Group 2

NF	Not allowed in spaces of Category A. Piping shall be laid in fire-resistant ducts vented to the atmosphere.
NEN, SN, ISO	Not allowed in spaces of Categories A, B and C. Piping shall be laid in fire-resistant ducts vented to the atmosphere (NEN), or eventually to the machinery room (SN and ISO).

BSI, NBN	Not allowed in spaces of Categories A, B, C and D. Piping shall be laid in fire-resistant ducts vented to the atmosphere (NBN), or eventually to the machinery room (BSI).
NK	Refrigerant piping in occupancy spaces of Category A: max. refrigerant charge of 250 kg. Refrigerant piping in occupancy spaces of Categories B and C: max. refrigerant charge of 500 kg. Piping shall be laid in ducts vented to the atmosphere.
ASHRAE, DIN, SK	No restrictions
Group 3	
BSI	Not allowed
NBN, NEN, SN	In occupancy rooms of Types A, B, C and D, use only in laboratories and up to a 2.5 kg refrigerant mass. In occupancy rooms of Type E, use is (more or less) unrestricted.
ISO	In occupancy rooms of Types A, B, C and D: in hallways, lobbies and sundry rooms, only hermetically sealed units of the absorption type with up to 2.5 kg refrigerant mass, but not in rooms where persons are restricted in their movement. In occupancy rooms of Type E, use is (more or less) unrestricted.
NK	Explosion safety precautions must be taken.
NF	Not allowed in occupancy rooms of Types A, B, C or D. In occupancy rooms of Type E, use is unrestricted although explosion safety precautions should be taken.
ASHRAE, DIN, SK	No restrictions.

In Japan, detailed regulations exist for each refrigerant group and nominal refrigeration capacity, depending on the configuration of the installation site.

A1.9 Marking - Certification - Instruction - Maintenance

This issue is absent in SN.

A1.9.1 Identification plate

Large pressure vessels shall be provided with a clearly visible identification plate (BSI, NBN, NEN, ISO, SK, NK, JN and NF). In DIN, reference is made to 'Technische Regeln Druckbehalter'.
Each refrigeration system, condenser unit, compressor unit etc shall be provided with an identification plate (BSI, NBN, ASHRAE, ISO, DIN, NK, NF).

A1.9.2 Operational instructions

A card placed conspicuously as near as is practicable to the refrigerant compressor shall give directions as to the operation of the system (NBN, NEN, ISO, DIN and NF). In SK and NK, a plate with some instructions shall be affixed to the door of the machinery room.

A1.9.3 Instruction manual

The manufacturer or installer shall supply with a refrigeration system one or more copies of an instruction manual (BSI, NBN, NEN, ISO, DIN, SK, NK, JN and NF).

A1.9.4 Summary

Table A1.8 gives an overview of Section A1.9. The presence of a regulation is indicated by an X;
absence by an O.

Table A1.8 Regulations on marking and instruction

	BSI	NBN	NEN	SN	ASHRAE	ISO	DIN	SK	NK	JN	NF
Identification plate	X	X	X	X	X	X	X	X	X	X	X
Operational instructions	O	X	X	O	O	X	X	X	X	O	X
Instruction manual	X	X	X	O	O	X	X	X	X	X	X

A1.10 Miscellaneous Special Requirements

A1.10.1 Pedestrian thoroughfares

Refrigeration systems shall not obstruct the free movement of persons in hallways and lobbies (BSI, NEN, SN, ASHRAE, ISO, DIN, SK and NK).

A1.10.2 Moving machinery

Fans and all moving machinery shall be guarded in accordance with health and safety regulations (BSI, NBN, NEN, SN, JN and ISO).

A1.10.3 Refrigerated spaces

Doors must open both from the inside and from the outside (BSI, NBN, NEN, ISO, SK, NK, JN and NF).

In the case of electrically or pneumatically operated doors, a means of opening the door by hand must be provided (BSI, NBN, NEN, ISO, SK, NK, JN and NF).

An alarm must be placed in the refrigerated room (BSI, NBN, NEN, ISO, SK, NK, NF and JN).

A1.10.4 Charging and discharging refrigerants

It is essential that full attention is given to the contents of service containers in order to prevent charging with the wrong substance, which could cause explosions or other accidents (BSI, NBN, NEN and NF).

Refrigerant shall be charged (by preference) into the low pressure side of the system ((BSI, NBN, NEN and ASHRAE).

In the case of discharging, the containers shall be carefully weighed during the transfer to prevent overfilling (BSI, ISO and DIN).

No refrigerant shall be discharged to a sewer, river or lake (BSI, NBN, NEN, ASHRAE, ISO and DIN).

Fully halogenated refrigerants shall be replaced by partially halogenated refrigerants during reconditioning and major repair work (SK and NK).

A1.10.5 Refrigerant stored in a machinery room

No refrigerant shall be stored in a machinery room apart from the charge in the system (BSI and NBN. ISO: up to 150 kg. JN: up to 100 kg).

A1.10.6 Repair

No repair work can be carried out until special precautions have been taken (BSI, NBN, NEN, ISO, SK and NF).

A1.10.7 Protective equipment

All standards prescribe protective equipment with the exception of SN.

A1.10.8 Noise

SK is the only standard dealing with noise.

A1.10.9 High pressure gases

The Japanese regulations have a lot of special requirements for high pressure gases.

A1.11 Evaluation and Conclusion

Table A1.9 contains an evaluation of the standards investigated. The specific items are compared in terms of their severity as well as of their comprehensiveness. A good safety standard has to be both strict and complete (no safety aspect neglected).

It should be clear, however, that this evaluation is based on only a limited number of regulations. It is also somewhat subjective in its approach.

Table A1.9 Evaluation of standards

Topic	BSI	NBN	NEN	SN	ASHRAE	ISO	JN	DIN	SK	NK	NF
Specific dangers	3	3	0	0	0	3	3	0	0	0	0
Scope	3	3	3	0	0	3	1	3	3	3	3
Small systems	3	3	3	0	0	3	3	0	3	3	2
HCFCs	0	3	0	0	3	0	0	3	3	3	0
Group 1	1	1	1	1	3	1	2	0	2	1	1
Group 2	3	3	3	3	3	3	3	0	3	3	3
Group 3	3	3	3	3	3	3	2	0	1	2	3
Standard pressure vessels	3	3	3	0	3	3	3	3	3	3	3
Strength repeat test	3	3	0	0	0	3	0	3	0	0	0
Pressure (general)	3	3	3	0	3	3	3	3	3	3	3
Machinery room	3	3	3	3	3	3	3	0	2	2	3
Alarm and detection	2	2	1	1	2	2	3	0	3	3	1
Electrical installation	2	3	2	2	3	2	3	0	2	2	2
Instrumentation	2	2	2	0	0	3	3	2	1	2	2
Materials and welding	3	3	3	0	3	3	3	3	3	3	1
Pipes and fittings	3	3	3	3	2	3	3	2	2	2	3
Marking, instruction and certification	2	3	3	0	1	3	2	3	3	3	3
Refrigerated spaces	3	3	3	0	0	3	3	0	3	3	3
Charging and discharging refrigerants	2	3	3	0	2	2	0	3	1	1	1
Safety provisions for personnel	3	3	3	0	1	3	2	1	3	3	1
Total	50/60	56/60	45/60	16/60	35/60	52/60	45/60	29/60	44/60	45/60	38/60

KEY		
	0	Item not treated in this standard
	1	Less elaborate/less restrictive treatment of topic
	2	Quite good treatment of topic
	3	Best possible treatment of topic

ANNEX 2
WORKING FLUID PROPERTIES

This Annex contains some of the physical and safety properties of about 120 refrigerants. A subdivision is made between the most commonly used refrigerants (Tables A2.1 and A2.2) and the less commonly used refrigerants (Tables A2.3 and A2.4).

Table A2.1 Most commonly used refrigerants: list of physical properties

Refrigerant name	Formula	Name	(g/mol) (Mol. weight)	(°C) Atm. boiling point	(bar) Sat. pressure	(kg/m^3) Density liquid
R10	CC14	tetrachloromethane	171	77	0.116	1600
R11	CC13F	trichlorofluormethane	137	24	0.881474	
R1113	CCIF=CF2	chlorotrifluorethene	117	-28	4.36	1300
R114	CCIF2-CCIF2	1,2-dichlorotetrafluorethane	171	4		
R1140	CHCI=CH2	vinyl chloride	63	-14	3.4	900
R115	CCIF-CF3	chloropentafluorethane	155	-39		
R1150	CH2=CH2	ethylene	28	-169.2	41	568
R116	CF3-CF3	Hexafluorethane	139	-78	29.67	
R12	CCI2F2	Dichlorodifluoromethane	121	-30	5.67	1488
R120	CCI3-CHI2	pentachloroethane	202	162	0.0045	1680
R123	CHCI2-CF3	2,2 dichloro 1,1,1-trifluoroethane	153	29		
R123a	CHCIF-CCIF2	1,2-dichloro-1,1,2-trifluoroethane	153			
R124	CHCIF-CF3	2-chloro-1,1,1,2-tetrafluoroethane	137	-12		
R124a	CHF2-CCIF2	1-chloro-1,1,2,2-trefluorethane	137	-10		
R125	CHF2-CF3	pentafluorotethane	120	-48		
R1270	CH3-CH=CH2	propene	42	-48	10.3	519.3
R13	CCIF3	chlorotrifluormethane	105	-81	31.73	921
R130	CHC92-CHCI2	1,1,2,2-tetrachloroethane	169	146	0.032	1600
R134a	CH2F-CF3	1,1,2,2-tetrafluoroethane	102	-26		
R13B1	CBrF3	bromotrifluoromethane	149	-58	14.4	1580
R14	CF4	carbon tetrfluoride	88	-128		1634
R140	CCI2H-CCIH2	1,1,2-trichloroethane	133	114	0.025	1400
R142	CH2CI-CHF2	2-chloro-1,1-difluoroethane	100	35		
R160	CH3-CH2CI	ethyle chloride	64	12	1.4	920
R21	CHCI2F	dichlorofluoromethane	103	9		
R216ca	CCIF2-CF2-CCIF2	1,3-dichloro-1,1,2,3,3, -hexafluoropropane	221	36		
R218	CF3-CF2-CF3	octafluoropropane	188	-37		
R22	CHCIF2	chlorodifluormethane	86	-41	9.1	1213
R23	CHF3	trifluormethane	70	-84	44.6	
R290	CH3-CH2-CH3	propane	44.1	-42.1	8.3	500
R30	CH2CI2	dichloromethane	85	41	0.44	1300
R40	CH3CI	chloromethane	50	-24	4.8	900
R500		73.8% R12 + 26.2% R152a	99	-33	4.4/4.9	<1000
R501		75.0% R22 + 25.0% R12	93	-41		
R502		48.2% R22 + 51.2% R115	112	-45	10.13	1200
R600	CH3-CH2-CH2-CH3	n-butane	58	-0.5	2.1	580
R600a	CH(CH3)3	i-butane	58	-12	3	600
R610	C2H5-O-C2H5	ethyl ether	74	35	0.587	710
R611	CH3-C00H	methyl formate	60	31	0.64	980
R630	CH3-NH2	methyl amine	31	-7	7.8	690
R631	CH3-CH2-NH2	ethyl amine	45	17	1.2	700
R717	NH3	ammonia	17	-33.4	8.572	680
R744	CO2	carbon dioxide	44	-79	57.3	
R764	SO2	sulphur dioxide	64	-10	3.305	1460
LiBr-powder	LiBr	lithiumbromide	86.8	1265		3465

Table A2.2 Most commonly used refrigerants: list of safety properties

Refrigerant name	(MJ/kg) Combustion heat	(°C) Flash point	(°C) Ignition temp.	(vol.%) LEL	(vol.%) UEL	(bar) Cnt. press.	(°C) Cnt. temp.	CAS	(ppm) TLV	(-) ODP
R10	/	/	/	/	/	45.585	283	56-23-5	10	0
R11	/	/	/	/	/	44.09	198	75-69-4	1000	1
R1113				24	40	40.63	106	79-38-9	/	
R114	/	/	/	/	/	32.627	145.7	76-14-2	1000	1
R1140		-78	472	3.8	31	55.9	156	75-01-4	5	0
R115	/	/	/	/	/	31.6	80	76-15-3	1000	0.6
R1150	47.25	-136	542	27	34	50.2	9.2	74-85-1	/	0
R116	/	/	/	/	/	29.8	19.7	86-16-4	/	
R12	/	/	/	/	/	41.15	112	75-71-8	1000	1
R120	/	/	/	/	/			76-01-7	5	0
R123	/	/	/	/	/				100	0.016
R123a	/	/	/	/	/				100	0.016
R124	/	/	/	/	/				500	0.02
R124a	/	/	/	/	/				500	0.02
R125	/	/	/	/	/			354-33-6	1000	0
R1270	45.88	-108	497	2	11	45.6	91.8	115-07-1		0
R13	/	/	/	/	/	38.73	28.85	75-72-9	/	0.45
R130	/	/	/	/	/		388	79-34-5	1	0
R134a	/	/	/	/	/				1000	0
R13B1	/	/	/	/	/	39.64	66.8	75-63-8	1000	10
R14	/	/	/	/	/	37.44	45.6	75-73-0	/	0
R140	/	/	/	/	/			79-00-5	10	0
R142										0
R160		-43	5	3.7	12	52	187	75-00-3	1000	0
R21	/	/	/	/	/	51.68	178.5	75-43-4	10	0.04
R215ca										
R218							26.8	71.9		
R22	/	/	/	/	/	49.77	96	75-45-6	1000	0.05
R23	/	/	/	/	/	48.1	26		/	0
R290	46.35	-104	468	2.1	9.5	42.5	96.8	74-98-6	/	
R30		/	556	/	/	60.78	237	75-09-2	500	0
R40		<0	632	8	18	66.5	143	74-87-3	50	0
R500									56275-41-3	
R501										
R502	/	/	/	/	/	59.73		39432-81-0		
R600	45.85	-60	405	1.8	8.4	37.97	152	106-97-8	800	
R600a				1.6	8.5	36.4	135	75-28-5	800	
R610		-45	180	1.9	48	36.0628	192.7	60-29-7	400	
R611		-32	46	4.5	20	59.969	214	107-31-3	100	0
R630		0	430	4.9	20.7	74.6	156.9	74-89-5	10	
R631		-18	384	3.5	14	56.3	183	74-04-7	10	
R717	18.48	gas	651	15	27	112.98	132.4	7664-41-7	25	0
R747	/	/	/	/	/	74	31	124-38-9	5000	0
R764	/	/	/	/	/	78.84	157.5	7446-09-5	2	0
LiBr-powder	/	/	/	/	/			7550-35-8		

Table A2.3 Most commonly used refrigerants: list of physical properties

Refrigerant Name	Formula	Name	(g/mol) Mol. weight	(°C) Atm. boiling point	(bar) Sat. pressure	(kg/m³) Density liquid
R110	CC13-CC13	Hexachloroethane	237	185	0.0006	2100
R111	CC12F-CC13	pentachlorofluoroethene	220	137		
R1110	CC12=CC12	tetrachlorethene	166	121	0.0173	
R1111	CC12=CC1F	trichlorofluoroethene	150			
R1112	CC1F-CC1F	1,2-dichlorodifluorethene	133	19		
R1114	CF2=CF2	tetrafluoroethene	100	-76		
R112	CC12F=CC12F	1,1,2,2-tetrachlorodifluorethane	204	93		
R1120	CC12-CHC1	trichlorethene	132	86	0.0773	
R1121	CC1H-CC1F	1,2-dichlorofluoroethene	115			
R1121	CHF=CC12	1,1-dichlorofluoroethene	115			
R1122	CHC1-CF2	1,1-difluorochloroethene	99	-19		
R1122a	CF2=CF2	1,2-difluorochloroethene	99			
R1123	CF2=CHF	trifluoroethene	82			
R112	CC13-CC1F2	1,1,1,2-tetrachlorodifluorethane	204	91		
R113	CC12F-CC1F2	1,1,2-trichlorotrifluoroethane	187	48	0.362	1560
R1130	CHC1=CHC1	1,2-dichlroethene (trans)	97	48	0.22	1257
R1130	CHC1=CHC1	1,2-dichloroethene (cis)	97	60	0.22	1280
R1130a	C2H2C12	1,1-dichloroethene	97	32	0.665	1250
R1131	CHC1=CHF	1-chloro-2-fluoroethene	81			
R1131a	CH2=CC1F	1-chloro-1-fluoroethene	81			
R1132	CHF=CHF	1,2-difluoroethene	64	-84		
R1132a	CH2=CF2	1,2-difluoroethene	64	-92		
R113a	CC13-CF3	1,1,1-trichlorotrifluoroethane	187	46		
R1141	CHF=CH2	vinyl fluoride	46	-71	25	700
R1141a	CC12F-CF3	1,1-dichlorotetrafluoroethane	171	4		
R121	CC12H-CC12F	1,1,2,2-tetrachlorofluoroethane	186	117		
R121a	CC13-CC1HF	1,1,1,2-tetrachlorofluoroethane	186	116		
R122	CC12H-CC1F2	1,2,2-trichloro-1,1-difluoroethane	169	72		
R122a	CC12F-CC1FH	1,1,2-trichloro-1,2-difluoroethane	169	73		
R122b	CC13-CHF2	1,1,1-trichlorodifluoroethane	169			
R123b	CC12F-CHF2	1,1-dichloro-1,2,2-trifluoroethane	153			
R12B1	CBrC1F2	bromochlorodifluoromethane	164			
R130a	CC13CC1H2	1,1,1,2-tetrachloroethane	169	131		
R131	CC12H-CC1FH	1,1,2-trichloro-2-fluorethane	151	103		
R131a	CC12F-CC1H2	1,1,2-trichloro-1-fluorethane	151			
R131b	CC13-CFH2	1,1,1-trichlorofluorethane	151	88		
R132	CHC1F-CHC1F	1,2-dichloro-1,2-difluoroethane	135	59		
R132a	CC12H-CHF2	1,1-dichloro-2,2-difluoroethane	135			
R132b	CC1H2-CC1F2	1,2-dichloro-1,1-difluoroethane	135	47		
R132c	CC12F-CH2F	1,1-dichloro-1,2-difluoroethane	118	17		
R133	CHC1F-CHF2	1-chloro-1,2,2-trifluoroethane	118			
R133a	CH2C1-CF3	2-chloro-1,1,1-trifluoroethane	118			
R133b	CC1FS2-H2F	1-chloro-1,1,2-trifluoroethane	118	12		
R134	CHF2-CHF2	1,1,2,2-tetrafluoroethane	102	-19		
R140a	CH3-CC13	1,1,1-trichloroethane	133	61	0.133	
R141	CC1HF-CC1HF	1,2-dichloro-1-fluorethane	116	76		
R141a	CH2F-CC12H	1,1-dichloro-2-fluorethane	116			

Table A2.3 Less commonly used refrigerants: list of physical properties (continued)

Refrigerant name	Formula	Name	(g/mol) Mol. weight	(°C) Atm. boiling point	(bar) Sat. pressure	(kg/m^3) Density liquid
R141b	CH3-CC12F	1,1-dichloro-1-fluorethane	116	9		
R142	CC1HF-CH2F	1-chloro-1,2-difluoroethane	100			
R142b	CH3-CC1F2	1-chloro-1,1-difluoroethane	100	-41		
R143	CH2F-CHF2	1,1,2-trifluoroethane	84	5		
R143a	CH3-CF3	1,1,1-trifluoroethane	84	-84		
R150	CC1H2-CC1H2	1,2-dichloroethane	99	84	0.133	
R150a	CH3-CHC12	1,1-dichloroethane	99	60		
R151	CH2C1-CH2F	1-chloro-2-fluoroethane	82	53		
R151a	CH3-CHC1F	1-chloro-1-fluoroethane	82	16		
R152	CH2F-CH2F	1,2-difluorethane	66	-31		
R152a	CH3-CHF2	1,1-difluorethane	66	-25		
R161	CH3-CH2F	ethyl fluoride	48	-78		
R170	CH3-CH3	ethane	30	-88.6	37.8	1355
R20	CHC13	trichloromethane	119	61		
R245cb	CF3-CF2-CH3	1,1,1,2-2-pentafluoropropane	134	-18		
R31	CH2FCl	chlorofluoromethane	69	-9		
R32	CH2F2	difluoromethane	52	-52		
R41	CH3F	flurometliane	34	-78		
R50	CH4	methane	16	-161.5		717.5
R503		40.1% R23 + 59.9% R13	87.5	-88		
R504		48.2% R32 + 51.8% R115	79	-57		
R505		78.0% R12 + 22.0% R31	103.5	-30		
R506		55.1% R31 + 44.9% R114	93.7	-12		
RC316	C4C12F6	1,2-dichlorohexafluorocyclobutane	233	60		
RC317	C4C1F7	chloroheptafluorocyclobutane	216.5	26		

Table A2.4 Less commonly used refrigerants: list of safety properties

Refrigerant name	(MJ/kg) Combustion heat	(°C) Flash point	(vol-%) Ignition temperature	(vol-%) LEL	(bar) UEL	(°C) Crit. pressure	Crit. temp.	(ppm) CAS	TLV	(-) ODP
R110	/	/	/	/	/			67-72-1	1	0
R111	/	/	/	/	/					
R1110	/	/	/	/	/		347	127-18-4	50	
R1111										
R1112										
R1114		<0	188	11	100	40.5	33	116-14-3	/	
R112	/	/	/	/	/	34.442	278	76-12-0	500	
R1120		32	410	7.6	90			79-0-6	50	
R1121										
R1121a										
R1122										
R1122a										
r1123										
R112a	/	/	/	/	/					
R113	/	/	/	/	/	34.15	214.1	76-13-1	1000	0.8
R1130		3.9	458	5.6	12.8	55.1208	243.3	156-60-5	200	0
R1130		6	458	6.2	16	55.1208	243.3	156-59-2	200	0
R1130a		-10	440	5.6	16			75-35-4	5	0
R1131										0
R113a										0
R1132				5.5	21					0
R1132a				5.5	21	44.3348	30.1			0
R113a	/	/	/	/	/				1000	0.8
R1141		<0	460	2.9	29	52.271	54.7	75-02-5	/	0
R114a	/	/	/	/	/	32.5	145.6	76-14-2	1000	1
R121	/	/	/	/	/					0
R121a	/	/	/	/	/					0
R122	/	/	/	/	/					0
R122a	/	/	/	/	/					0
R122b	/	/	/	/	/					0
R123b	/	/	/	/	/				100	0.016
R12B1	/	/	/	/	/	42.5	154			3
R130a	/	/	/	/	/					0
R131	/	/	/	/	/					0
R131a	/	/	/	/	/					0
R131b	/	/	/	/	/					0
R132	/	/	/	/	/					0
R132a	/	/	/	/	/					0
R132b	/	/	/	/	/					0
R132c	/	/	/	/	/					0
R133	/	/	/	/	/					0
R133a	/	/	/	/	/		150			0
R133b	/	/	/	/	/					0
R134	/	/	/	/	/					0
R140a	/	/	/	/	/			71-55-6	350	0

Table A2.4 Less commonly used refrigerants: list of safety properties (continued)

Refrigerant name	(MJ/kg) Combustion heat	(°C) Flash point	(vol-%) Ignition temperature	(vol-%) LEL	(bar) UEL	(°C) Crit. pressure	Crit. temperature	(ppm) CAS	TLV	(-) ODP
R141										0
R141a										0
R141b									500	0
R142a										0
R142b				4.4	18.5	41.16	137		/	0
R143									/	0
R143a				9.2	18.4	37.53	73		/	0
R150		150	413	6.2	16	50.65	288	107-06-2	10	0
R150a		-5.6	458	5.6	16	50.662	250	75-34-3	200	0
R151										0
R151a										0
R152										0
R152a						44.9	113.5			0
R161										0
R170	47.49	gas	530	3	15.5	48.8	32	74-84-0	/	
R20	/	/	/	/	/	54.702	263	67-66-3	10	0
R245cb										
R31										0
R32						58.3	78.4			0
R41						59.74	45			0
R50	50.14	-188	538	5	15	46	-82.5	74-82-8		
R503	/	/	/	/	/					
R504										
R506										
RC316										
RC317										

ANNEX 3
CALCULATION PROGRAMME DESCRIPTIONS

This Annex provides an overview of the models which are implemented in Microsoft Excel 4.0 for calculating the effects of accidents with working fluids.

The calculation programs reside and are maintained at the University of Leuven. Use and availability of the programs has to be discussed with the lead author of this report:

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A standardised sheet is provided for each model. This lists information regarding the calculation procedure, the assumptions, the required input, the output obtained and the validity range, together with some remarks.

The following subroutines are discussed:

- gas concentration in a room or apparatus;
- working fluid emission rate for a gas release;
- working fluid emission rate for a liquid release;
- working fluid emission rate for a two-phase release;
- evaporation of boiling liquids;
- evaporation of non-boiling liquids;
- initial flash fraction;
- jet flame;
- pool fire;
- fire-ball;
- explosive expansion of a compressed gas;
- boiling liquid expanding vapour explosion (BLEVE);
- vapour cloud explosion;
- heavy gas dispersion;
- neutral gas dispersion;
- vulnerability: overpressure, heat radiation and toxic gases.

A database containing the properties of the working fluids is provided with these subroutines. Other working fluids can be added.

Effect evaluation	Gas concentration in a room or apparatus
Calculation procedure	For an instantaneous or continuous emission of working fluid inside a room the concentration of the working fluid is calculated as a function of time. The remaining oxygen concentration is found at the same time.
Assumptions	• Based on experiments it has been found that the concentration in a room can be regarded as homogeneous due to the effect of natural ventilation. Therefore buoyancy forces are not taken into account. • When ventilating, no density difference between the outside and inside air is assumed. • The concentration of the working fluid is only reduced as a result of air exchange. Conservatively, no adsorption or chemical reactions of the working fluid inside the room are taken into account. • Continuous emissions of working fluid are at a constant emission rate. • Density of the released working fluid is taken at room temperature.
Required input	• Released working fluid • Type of release : - instantaneous - continuous • Amount released (inst. release) release rate (cont. release) • Degree of ventilation : - air exchange rate in m3/h - ventilation degree in 1/h - ventilation degree = f(windsp., type of building) • Total volume of the room • Temperature in the room
Output obtained	• Concentration of working fluid in the room as a function of time • Concentration of oxygen in the room as a function of time • If the fluid is toxic, the equivalent concentration of exposure is calculated
Validity range	• As a homogeneous concentration is assumed the results will only be valid for a room where enclosure of the gas at specific places will not occur.
Remarks	• The maximum concentration of a working fluid (or the minimum concentration of oxygen) in a room or apparatus, eg. refrigerator can be calculated by assuming the air exchange rate = 0. • The minimum end time for calculation = 60 s / the minimum time step = 5s.

Effect evaluation	Working fluid emission rate for a gas release
Calculation procedure	The emission rate of working fluid is calculated for a gas jet release from a pressurised tank. The calculation is also valid if the discharge from the tank is through a short pipe (as long as frictional pressure losses are can be ignored).
Assumptions	• The release rate is constant, i.e. the pressure in the tank is assumed to be constant. • The discharge coefficient equals 0.61 (the discharge coefficient for a round hole in a vessel). If for some reason the discharge coefficient has a larger value, the release rate has to be multiplied by this value and divided by 0.61. • No heat exchange during release is assumed (adiabatic process). • Release in atmosphere (i.e. atmospheric pressure outside the tank).
Required input	• Released working fluid • Pressure in tank: given pressure saturation pressure (at 20°c) • Diameter of opening
Output obtained	• Release rate
Validity range	• Release rates through pipes are only valid for short pipes. For longer pipes the calculated release rate will be an overestimation because frictional effects are not taken into account. If F x L / d > 0.25, frictional effects become important (F = Fanning friction coefficient, L = pipe length and d = diameter of pipe). (as a rule of thumb frictional effects become important for a pipe length = 100 x diameter) • A distinction is made between critical and subcritical flow.
Remarks	• The discharge coefficient of a round hole in the wall of a vessel has a discharge coefficient of appr. 0.61. For the release from a tank through a short pipe where the release-opening is also round, the same discharge coefficient (= 0.61) can be used.

Effect evaluation	Working fluid emission rate for liquid release
Calculation procedure	The emission rate of working fluid is calculated for a fluid release from a tank. The calculation is also valid if the discharge from the tank is through a short pipe (as long as frictional losses can be ignored).
Assumptions	• The release rate is constant, i.e. the pressure in the tank is assumed to be constant. • The discharge coefficient equals 0.61 (the discharge coefficient for a round hole in a vessel. • No heat exchange during release is assumed (adiabatic process). • The discharge coefficient equals 0.61 (the discharge coefficient for a round hole in a vessel). • Release into atmosphere (i.e. atmospheric pressure outside the tank).
Required input	• Released working fluid • Pressure in tank: - given pressure - saturation pressure (at 20°c) • Liquid height above hole • Diameter of opening
Output obtained	• Release rate
Validity range	• Release rates through pipes are only valid for short pipes. For longer pipes the calculated release rate will be an overestimation because frictional effects are not taken into account. If F x L / d > 0.25, frictional effects become important (F = fanning friction coefficient, L = pipe length and d = diameter of pipe). • Only constant release rates are calculated.
Remarks	• If one wants to calculate the release of a liquid from a tank as a function of the changing height of the liquid in the tank, this calculation has to be executed for different steps in time where one uses as input the changing liquid height. • When choosing the saturation pressure at 20°c as the pressure in the tank, the minimum pressure is assumed to be the atmospheric one.

Effect evaluation	Working fluid emission rate for two-phase release
Calculation procedure	The emission rate of working fluid is calculated for a two-phase jet release from a pressurised tank. The initial amount that flashes (adiabatic expansion) is also determined.
Assumptions	• Constant pressure in the tank • Homogeneous two-phase flow. • Thermodynamic equilibrium in the flashing mixture. • Thermal equilibrium in the non-flashing mixture. • Isenthalpic expansion process for the flashing mixture. • Isothermal expansion process for the non-flashing mixture. • Ideal gas behaviour of the vapour. • Release in atmosphere (atmospheric pressure and atmospheric temperature of 20°C outside the tank). • Temperature of the fluid in the tank = 20°c
Required input	• Released working fluid • Diameter of opening • Vapour fraction just before the opening
Output obtained	• Release rate • Initial flash fraction (adiabatic expansion)
Validity range	• The release of a liquid from a tank can only result in a two-phase flow if the two phase flow can develop in a short pipe (10cm). If the release is through a hole in the vessel wall, there will be a release of liquid (and flashing occurs outside the tank). The release rate of pure liquid will be higher compared with the two-phase flow release rate. • Release rates through pipes are only valid for short pipes. For longer pipes the calculated release rate will be an overestimation because frictional effects are not taken into account. • Only constant release rates are calculated.
Remarks	• The saturation pressure, heat of evaporation,specific heat and density of the liquid in the database are given at a temperature = 20°c. As the calculation of the two-phase release rate is very sensitive to the properties of the working fluid, the result obtained is only valid for a release at 20°c and at saturation pressure. Calculation of the release rate at higher pressures (but also 20°c) can be executed, but the results are less accurate.

Effect evaluation	Evaporation of boiling liquids
Calculation procedure	The evaporation rate of a pool of boiling liquid is calculated
Assumptions	• The evaporation is mainly determined by the heat conduction from the soil to the liquid • An non-porous soil is assumed
Required input	• Released working fluid • Soil type: non-permeable - average soil (8% water content) - concrete - porous - moist soil (8% water content) - dry sand • Temperature of the fluid • Temperature of the soil • Area of the pool
Output obtained	• Evaporation rate as a function of time • If the fluid temperature is higher than the atmospheric boiling point, the initial flash fraction is calculated
Validity range	• Liquid pools on water are not taken into account. • The evaporation rate is rapidly decreasing in time. One has to check if the evaporation rate for the non-boiling situation doesn't exceed the evaporation rate of the boiling liquid. The highest of the two should be taken.
Remarks	• The programmes for evaporation of boiling and non-boiling liquids are integrated in one module. The choice is made automatically as av function of the given temperatures (of soil and liquid) and the atmospheric boiling point of the chosen working fluid. • If the given temperature exceeds the atmospheric boiling point, one assumes flashing will take place. The remaining liquid will cool to atmospheric boiling point. • For a porous soil the calculation is strictly valid for liquid LNG pools (methane). It provides, however, ann estimate for liquids with an atmospheric boiling point , freezing point of water.

Effect evaluation	Evaporation of non-boiling liquids
Calculation procedure	The evaporation rate for a non-boiling liquid pool is calculated
Assumptions	• The evaporation is mainly determined by the difference between the saturation pressure of the liquid and the atmospheric pressure (diffusion process) • Isothermic evaporation is assumed under neutral atmospheric conditions. • Circular as well as square pools are considered • Wind speed is taken at 10 m above the earth's surface. • Obstacles disturbing the wind profile are assumed not to be present near the pool.
Required input	• Released working fluid • Area of pool surface • Pool shape: - square - circular • Windspeed (at 10 m) • Partial pressure of the working fluid at the liquid surface • Temperature of the liquid (see remark)
Output obtained	Evaporation rate
Validity range	• Windspeed must be > 1 m/s • The calculated evaporation rate is valid at the beginning of the evaporation process (before liquid pool has cooled down) and is thus a maximum (conservative result).
Remarks	• The programmes for evaporation of boiling and non-boiling liquids are integrated in one module. As a function of the given temperature and the atmospheric boiling point, this choice is automatically made. • The temperature of the liquid is also used to determine if the pool is boiling or not. If not, and if the temperature = 20°c, the saturation pressure is taken as the partial pressure of the liquid.

Effect evaluation	Initial flash fraction
Calculation procedure	The amount of a liquefied gas that flashes upon release is calculated.
Assumptions	• The flashing is assumed to occur adiabatically • The specific heat and the heat of evaporation are assumed to be constant.
Required input	• Released working fluid • Temperature of liquified gas
Output obtained	• Initial flash fraction (as a mass-fraction of the amount released)
Validity range	• The heat of evaporation of the flashing process is only taken from the released (remaining) liquid phase. • The initial flash fraction is calculated for: - evaporation of liquids - two-phase release.
Remarks	

Effect evaluation	Jet flame
Calculation procedure	The heat radiation of a jet flame is calculated for a vertical gas jet release.
Assumptions	• The heat radiation is calculated assuming a point source model at the centre of the flame (halfway along the centre line from the nozzle to the tip of the flame). • A turbulent jet flame is assumed. • Atmospheric heat absorption is not taken into account. • Maximum incident heat flux is assumed with respect to the inclination of the exposed object.
Required input	• Released working fluid • Height of release opening with respect to ground level • Diameter) of opening • Pressure in the tank • Windspeed (or no wind)
Output obtained	• Length of jet flame / inclination of flame • Heat radiation vs distance: - downwind - upwind
Validity range	• If windspeed assumed then : $u_w \geq 1$ m/s. • The pressure in the tank must be > 2 bar to always obtain a critical release. • Only vertical jet flames are taken into account.
Remarks	

Effect evaluation	Pool fire
Calculation procedure	The dimensions of the flame of a pool-fire are calculated The heat radiation from the flame is calculated.
Assumptions	• For a continuous spill the maximum area of the pool at equilibrium is assumed. • A constant burning rate is assumed. • Burning rates are estimated assuming a spill on land. • Flame geometry : circular or tilted cylinder. • The heat radiation is calculated stating from the maximum heat flux at the surface of the flame. • Atmospheric absorption is conservatively not taken into account.
Required input	• Released working fluid • Spill type : - confined spill - unconfined spill • For confined, instantaneous spill : area of confinement • For unconfined, continuous spill : release rate • Wind speed • Heat flux at surface of the flame.
Output obtained	• Mass burning rate of working fluid • Equivalent pool diameter (confined spill) • Equilibrium pool diameter (unconfined spill) • Heat radiation: - downwind - upwind • Flame height • Flame drag at the base of the flame • Flame tilt
Validity range	• The diameter of the pool must be at least 1 m. • For a confined spill the equivalent diameter (diameter of circular pool with same area) is used for the calculations.
Remarks	• For spills on water, the burning rate will be similar to the one for spills on land if the atmospheric boiling point of the fluid is above ambient temperature. For other liquids the burning rate is higher as a result of a higher heat transfer rate between the water and the pool. For liquifiedc gases the burning rate on water is typically twice that on land.

- For an instantaneous spill an unconfined pool fire grows in size until a barrier is reached or until all the 'fuel' is consumed. If unconfined, with no barriers, the maximum diameter will only exist for a very short time and use of this maximum diameter will result in very conservative results. Therefore the area of the pool should be known to obtain reliable results.
- The average surface emissive power at the flame surface can be estimated with the aid of two correlations: sooty or non-sooty fires.
- The equilibrium diameter for an unconfined spill (continuous release) is found when the release rate is equal to the burning rate over the total pool area.
- A minimum distance for the calculation of the heat radiation is automatically taken into account.

Effect evaluation	Fire-ball
Calculation procedure	The maximum diameter and the heat radiation of a fire-ball are calculated.
Assumptions	• Atmospheric heat absorption is conservatively not taken into account. • The growth of the fire-ball and also its rising effect are taken into account for the calculation of the heat radiation. • The heat radiation is calculated assuming a point source model.
Required input	• Released working fluid • Total amount released • Distance(s) for evaluating heat radiation
Output obtained	• Maximum diameter of fire-ball • Heat radiation at given distances as a function of time. • Equivalent heat intensity (constant intensity over the same exposure time where the same effects on people can be expected).
Validity range	• A fire ball assumes the instantaneous release of a liquefied gas under pressure.
Remarks	• To calculate the effects of exposure to heat radiation an equivalent heat radiation intensity is calculated for the exposure time. Exposure to this equivalent heat radiation has the same effects on people as on the real varying intensity.

Effect evaluation	Explosive expansion of a compressed gas
Calculation procedure	The peak overpressure resulting from the expansion of the compressed gas is calculated.
Assumptions	• An isothermal/isentropic expansion of the gas is assumed. • Overpressures are found on basis of TNT-equivalence. This is valid if the vessel disintegrates fast. • Brittle or ductile fracture (resp. 80% or 40% of the isentropic expansion energy assumed to be found in the generated pressure waves). • The presence of a reflecting surface (amplification of the blast wave) can be taken into account.
Required input	• Released working fluid • Amount of gas in vessel • Pressure in vessel at time of rupture • Brittle or ductile fracture • Presence of a reflecting surface • Distances for evaluation
Output obtained	Peak overpressure vs. distance (from vessel)
Validity range	The vessel disintegrates
Remarks	• One has to take into account the effects of fragmentation. • The pressure in the vessel at the time of disintegration must be > 2 bar. • If the distances for evaluation are too small they are automatically changed. In that case the distances where the overpressure is between 0.02 and 1 bar are taken into account.

Effect evaluation	Boiling liquid expanding vapour explosion (BLEVE)
Calculation procedure	The peak overpressure resulting from the expansion of the boiling liquid is calculated.
Assumptions	• An isentropic expansion of the working fluid is assumed. • Estimation of the isentropic expansion energy is on the basis of the difference between the temperature of the liquid and its atmospheric boiling point on the one hand, and the volume of the liquid phase in the vessel on the other hand. • To determine the expansion energy the properties of propane are assumed as an estimate. • Peak overpressures are found on the basis of TNT-equivalence. This is valid if the vessel disintegrates fast. • Brittle or ductile fracture (respectively 80% or 40% of the isentropic expansion energy (assumed to be found in the generated pressure waves). • The presence of a reflecting surface (amplification of the blast wave) can be taken into account.
Required input	• Released working fluid • Contents of the vessel • Amount of liquid phase in the vessel • Temperature of fluid when vessel bursts • Brittle or ductile fracture • Presence of reflecting surface (e.g. earth surface) • Distance for evaluation
Output obtained	Peak overpressure vs distance
Validity range	The calculated overpressure is more adequate at large distances from the vessel.
Remarks	• If a flammable liquid is released and an immediate ignition occurs, the effects of a fire-ball also have to be taken into account. • Atmospheric pressure is assumed outside the vessel. • If a flammable fluid is released and immediately ignited the effects of a fire ball also have to be taken into account. • If the distances for evaluation are too small they are automatically changed. In that case the distances where the overpressure is between 0.02 and 1 bar are taken into account. • If the critical temperature is < 20°c, a BLEVE can only be expected at a temperature below the critical temperature. This calculation cannot be executed within this program.

Effect evaluation	Vapour cloud explosions
Calculation procedure	The peak overpressure resulting from semi-confined and unconfined vapour cloud explosions is calculated.
Assumptions	• Overpressures are found on basis of TNT-equivalence. • For an unconfined vapour cloud explosion (UVCE) the efficiency of the explosion (ratio of the energy in the blast wave to the energy theoretically available from the heat of combustion) is taken as a function of the explosive mass in the cloud. An estimate of the ignition and explosion probability as a function of explosive mass is given as well. These correlations are based on observations. • The presence of a reflecting surface (e.g. earth surface) can be taken into account. • For a semi-confined cloud (between process installations, buildings etc.) a constant efficiency is assumed.
Required input	• Working fluid in cloud • Unconfined or semi-unconfined cloud • Total explosive mass in cloud • Presence of a reflecting surface
Output obtained	• Peak overpressure vs. distance from centre of cloud • Efficiency of the explosion • Ignition probability (UVCE) • Explosion probability (UVCE)
Validity range	• Relevant overpressures for unconfined vapour cloud explosions require that a minimum amount of flammable gas is present between the explosion limits at the time of ignition. If the explosive mass is too small a burning cloud will occur without overpressure in the surroundings. The probability of an explosion with an explosive mass of less than 1 ton is less than 1%. • The minimum explosive mass must be > 100 kg.
Remarks	• The distinction between an unconfined and a semi-confined vapour cloud depends on whether or not it is appropriate to assume a dispersion over a flat terrain with no obstacles. If a dispersion of that kind can be assumed one has to take into account an unconfined vapour cloud. • The overpressures from a UVCE are limited to some tenths of a bar (deflagration). • If the distances for evaluation are too small they are automatically changed. In that case the distances where the overpressure is between 0.02 and 0.2 bar are taken into account.

Effect evaluation	Heavy gas dispersion
Calculation procedure	The distance area where a concentration between 1 and 10 vol% can be expected is calculated for an instantaneous or continuous release of working fluid.
Assumptions	• The dispersion area is a flat terrain (no obstacles). • The downwind distance where the concentration of interest can be expected is calculated for a mean and a worst situation. • Continuous release occurs with a constant release rate. • The initial concentration is 100%.
Required input	• Released working fluid • Type of release : cont./instant release • Released rate (cont. release) • Release amount (inst. release) • Release state : - gas - gas liquified without pressure - gas liquified by pressure - gas liquified by pressure like NH_3 • Temperature of the working fluid for release state : - gas - gas liquified without pressure
Output obtained	• Downwind distance vs concentration at ground level (mean and worst situation) • Guideline for the toxicity of the fluid (if applicable) • Range of the explosive mass for a continuous release
Validity range	• For an instantaneous release the initial released volume must be $> 0.1\ m^3$ • For a continuous release the initial release rate by volume must be $> 10^{-3}\ m^3/s$. • Release must be near ground level. • Modelling of the dynamic and thermodynamic processes when the fluid is released are not included. It is assumed that, near the source, these processes are terminated after release.
Remarks	• Influence of obstacles - with obstacles which obstruct the lateral dispersion (eg. walls which are parallel to the wind) higher concentrations can be expected downwind in comparison with the case of dispersion without obstacles. - with obstacles which result in an intensification of the lateral or vertical mixing (eg. protection walls vertical to the wind direction) lower concentrations can be expected downwind in comparison with the case of dispersion without obstacles. • Gases like ammonia can form heavy gas clouds if very cold. • For concentrations < 1 vol% the dispersion of a heavy gas modelled like a neutral gas. • The distances for the calculation are chosen automatically. • For an instantaneous release the maximum explosive mass can be estimated at about 2/3 of the released mass.

Effect Evaluation	Neutral gas dispersion
Calculation procedure	The concentration at downward distances is calculated for an instantaneous or continuous release of working fluid.
Assumptions	• The dispersion area is a flat terrain (no obstacles). • Continuous release occurs with a constant release rate.
Required Input	• Released working fluid • Type of release: cont./Instant. release • Amount released (inst. release) • Type of terrain (5 types) • Wind speed • Stability class (Pasquill- D or F)
Obtained output	• Downward distance vs. concentration at ground level • For an instantaneous release of a toxic fluid the equivalent toxic concentration and exposure time is calculated • Explosive mass in the cloud
Validity rang	• Release must be near ground level from a point source. • Modelling of the dynamic and thermodynamic processes within the fluid is released are not included. • The calculation of the explosive mass in the cloud assumes a spherical cloud.
Remarks	• If the density of the gas is < 1.4 kg m_3, it is assumed to be a neutral gas (except for gases like ammonia). • Dispersion of heavy gas followed by a neutral phase, the heavy gas followed by a neutral phase, the heavy gas dispersion phase assumes the worst dispersion situation. • For the instantaneous release of a heavy gas followed by a neutral phase, the heavy gas dispersion phase is calculated using a simple box model.

Effect evaluation	Vulnerability: exposure to overpressure, heat radiation or toxic gases
Calculation procedure	The probability of death or severe injury as a result of overpressure, heat radiation or exposure to toxic gases is calculated.
Required input	• Kind of effect: - overpressure (1) - heat radiation (2) - toxic gases (3) • If (1): overpressure of interest • If (2): heat radiation and period of exposure • If (3): (toxic) working fluid and concentration and period of exposure
Output obtained	• If (1): probability of death, eardrum rupture and death by lung haemorrhage • If (2): probability of death and of 1st and 2nd degree burns • If (3): probability of death • Guidelines for a probability of 1%, 50% and 99%
Validity range	• The calculated risks are a rough, conservative estimates that hold for average people. This is particularly the case for the lethal effects for exposure to toxic gases. • The lethal effects of exposure to toxic gases refer to the effects resulting from inhalation.
Remarks	• For buildings the probability of glass breaking and structural damage are calculated as well.